DATA ON NATURAL ORGANIC SUBSTANCES IN DISSOLVED, COLLOIDAL, SUSPENDED-SILT, AND-CLAY AND BED-SEDIMENT PHASES IN THE MISSISSIPPI RIVER AND SOME OF ITS TRIBUTARIES, 1991-92

by J.A. Leenheer, L.B. Barber, C.E. Rostad, and T.I. Noyes

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CONTENTS

	Ct
	uction
	Acknowledgments
	August 1991 cruise
	Objectives and approach
	Dissolved organic matter
	Organic matter in suspended-sediment fractions
Septer	nber-November 1991 cruise
	Objectives and approach
	Dissolved organic matter
	Organic matter in suspended-sediment fractions
March	-May 1992 cruise
	Objectives
	Dissolved organic matter
	Organic matter in suspended-sediment fractions
Organ	ic matter in bed sediments
	nal variation
	Dissolved organic matter
	Organic matter in suspended-sediment fractions
	isions
	nces cited
3.	Mississippi River as a function of river miles upstream from Head of Passes, La., for the summer, fall, and spring 1H-nuclear magnetic resonance (NMR) spectrum of dissolved organic matter isolated from the Mississippi River at Hastings, Minnesota, during the April-May 1992 (spring) sampling cruise
TABL	
1.	Dissolved organic-carbon concentrations for samples collected during the upriver part of the June-August 1991 cruise
2.	Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the June-August 1991 cruise
3.	Concentrations of silt and clay and colloid fractions of suspended sediment and organic-carbon concentrations of these fractions for samples collected during the downriver part of the June-August 1991 cruise
4.	Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment for samples collected during the downriver part of the June-August 1991 cruise
5.	Organic-carbon and nitrogen transport of the silt and clay and colloid fractions for sediment samples collected during the downriver part of the June-August 1991 cruise
6.	Dissolved organic-carbon concentrations for samples during the upriver part of the September-November 1991 cruise
7.	Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the September-November 1991 cruise
8.	Concentrations of silt and clay and colloid fractions of suspended sediment, and organic-carbon concentrations of these fractions for samples collected during the downriver part of the September-
	November 1991 cruise

9.	Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment for samples collected during the downriver part of the September-November 1991 cruise	26
10.	Organic-carbon and nitrogen transport of the silt and clay and colloid fractions for sediment samples collected during the downriver part of the September-November 1991 cruise	27
11.	Dissolved organic carbon concentrations for samples collected during the upriver part of the March-May 1992 cruise	28
12.	Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the March-May 1992 cruise	33
13.	Concentrations of silt and clay and colloid fractions of suspended sediment, and organic-carbon concentrations of these fractions for samples collected during the downriver part of the March-May 1992 cruise	36
14.	Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment for samples collected during the downriver part of the March-May 1992 cruise	37
15.	Organic-carbon and nitrogen transport of the silt and clay and colloid fractions for sediment samples collected during the downriver part of the March-May 1992 cruise	38
16.	Organic-carbon and nitrogen contents of bed-sediment	39
17.	Organic-carbon and nitrogen percentages of bed sediment samples and suspended silt and clay samples	41
18.	Peak height ratios for ¹ H -NMR data for dissolved organic-carbon samples collected during the September-November 1991 (fall) and March-May 1992 (spring) sampling cruises	45

CONVERSION FACTORS AND RELATED INFORMATION

Multiply	Ву	To obtain
liter (L)	0.2642	gallon
cubic meter per second (m ³ /s)	35.31	cubic foot per second
kilometer (km)	0.6214	mile
cubic kilometers (Km ³)	0.2399	cubic miles
micrometer (μm)	0.00003937	i nc h
milligrams (mg)	0.00003527	ounce, avoirdupois
metric tons per day	1.102	short tons per day
milligrams per liter	0.0001335	ounce per gallon

Proton Nuclear Magnetic Resonance (¹H-NMR) Units

chemical shift [δ in

Equals

chemical shift ($\tau = 10 - \delta$)

parts per million (ppm)]

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation: $^{\circ}F = (1.8 \times ^{\circ}C) + 32.$

Data on Natural Organic Substances in Dissolved, Colloidal, Suspended-Silt and -Clay, and Bed-Sediment Phases in the Mississippi River and Some of its Tributaries: 1991–92

By J.A. Leenheer, L.B. Barber, C.E. Rostad, and T.I. Noyes

Abstract

The Mississippi River and some of its tributaries were sampled for natural organic substances dissolved in the water and in suspended and bed sediments during three sampling cruises in 1991 and 1992. Sampling for water and sediment was conducted from a research vessel from near Minneapolis, Minnesota to near New Orleans, Louisiana. Samples for dissolved organic carbon were collected as the vessel cruised upriver from New Orleans, and water and sediment samples were collected on the downriver part of the sampling cruise. The first cruise occurred during June–August, 1991; the second cruise occurred during September–November, 1991; and the third cruise occurred during March–May, 1992. The purpose for sampling and characterizing natural organic substances in the various phases in the river was to gain an understanding of how these substances facilitate contaminant transport and transformation in the Mississippi River. The study was done in cooperation with associated research projects studying transport of specific contaminants.

Significant findings of the study include the following: (1) There are large nitrogen contents (1.5 to 2.0 times normal) in the suspended and bed sediments of the Upper Mississippi River. These large nitrogen contents may cause toxic levels of ammonia resulting from microbial decomposition of nitrogen-containing organic matter in anaerobic bed sediments. (2) Organic-carbon contents of suspended colloids in the Upper Mississippi River were 2 to 3 times the organic-carbon content of suspended colloids in the Lower Mississippi River. This high organic-carbon content enhanced the transport of organic contaminants such as polychlorinated biphenyls that partition into organic matter. (3) Colloidal organic matter was transported conservatively through the navigation pools of the Upper Mississippi River. Transport calculations showed very little of the colloidal organic matter is being lost in the deeper navigation pools (Lake Pepin and Pool 19) that serve as sediment traps. (4) Organic matter in the dissolved, suspended, and colloidal phases decrease in a downstream direction. This decrease is caused by dilution by tributaries low in organic-matter concentrations and by instream losses of organic matter during transport. Evidence for instream biodegradation of organic matter was found during the summer cruise; this degradation may release bound contaminants back to the more toxic dissolved state in water.

INTRODUCTION

The Mississippi River drains about 40 percent of the conterminous United States and commonly is divided into two parts—the Lower Mississippi River and the Upper Mississippi River. Distances on the Lower Mississippi River begin at zero where the mouth of the river divides into three separate channels at Head of Passes in Louisiana and increase upstream to the mouth of the Ohio River at Cairo, Illinois (Lower Mississippi River Mile 953.8). Distances on the Upper Mississippi River begin at zero at the mouth of the Ohio River and increase upstream to the source of the Mississippi River in Minnesota (fig. 1). The Lower and Upper Mississippi Rivers are very different in hydrologic character. The Lower Mississippi River is a free flowing river, whereas about 80 percent of the navigable length of the Upper Mississippi River is controlled by a series of 29 navigation locks and dams, creating a stair-step series of navigation pools.

The mean annual water discharge of the Mississippi River increases from about $7 \text{ km}^3/\text{yr}$ near Minneapolis, Minnesota to about $500 \text{ km}^3/\text{year}$ at Vicksburg, Mississippi (period of record 1931-1991), while the corresponding sediment discharge increases from about 0.2×10^6 metric tons/year to about 200×10^6 metric tons/year. The mean

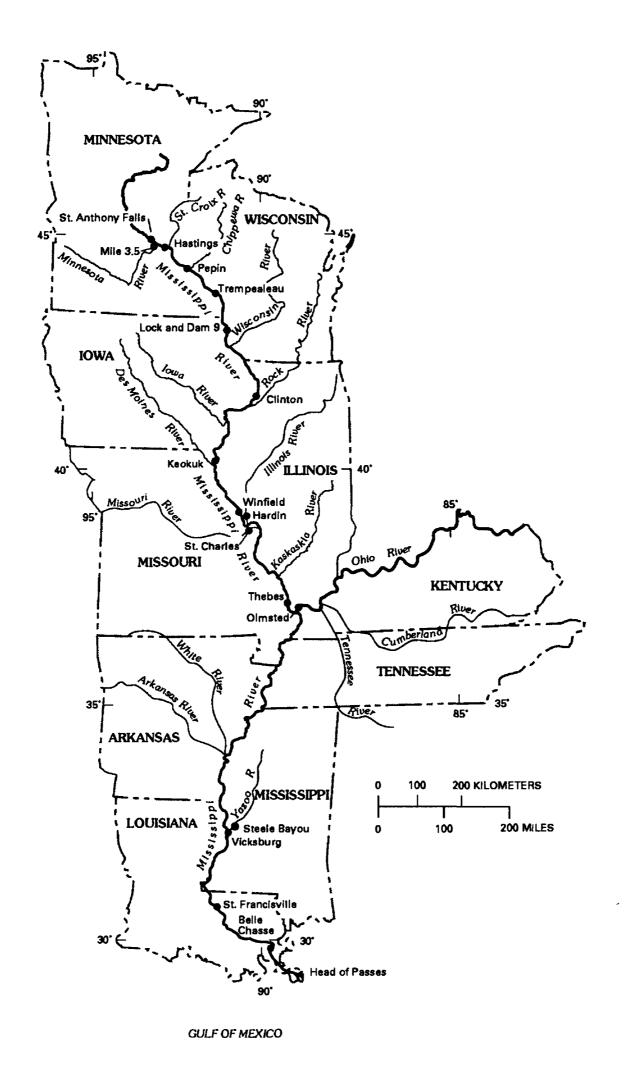


Figure 1.--Location of sampling sites on the Mississippi River and some of its tributaries.

annual water discharge of the Mississippi River more than doubles with the addition of water from the Minnesota and St. Croix Rivers just downstream from Minneapolis, Minnesota. The mean annual discharge of the river increases slowly with each tributary input until the combined water discharges of the Illinois and Missouri Rivers more than doubles the discharge of the Upper Mississippi River to about 160 km³/year. The addition of water from the Ohio River again doubles the discharge of the Mississippi River; both the contributions of water by the White and Arkansas Rivers (each having discharges 2 to 5 times greater than the combined flow of the Minnesota and St. Croix Rivers) only account for about 5 to 8 percent of the discharge of the Lower Mississippi River at Vicksburg, Mississippi. At 191 kilometers downstream from Vicksburg, approximately 25 percent of the water discharge and sediment discharge is diverted from the Mississippi River by the Old River control structure into the Atchafalaya River and then into the Gulf of Mexico. The remaining water (375 km³/year) and sediment (150 × 10⁶ metric tons/year) are discharged by the Mississippi River directly into the Gulf of Mexico (Moody and Meade, 1992).

Most contaminants have some degree of association with natural organic substances in the dissolved, colloidal, and particulate phases in water (Leenheer, 1991; Leenheer and others, 1994). These associations may either facilitate or retard contaminant transport in rivers and may transform contaminants into different phases or different compounds depending on the operative degradation processes. The U.S. Geological Survey began a study of contaminant assessment and transport in the Mississippi River and some of its tributaries in 1987.

This report summarizes the research on natural organic substances that was conducted during three sampling cruises on the Mississippi River between Minneapolis, Minn., and New Orleans, La., between June 1991 and May 1992. Although the sampling encompassed the entire river, the intensity of the sampling was much greater on the Upper Mississippi River upstream from St. Louis, Mo., because a previous study (Leenheer and others, 1995) performing similar research was conducted on the Lower Mississippi River from 1987–90. Integration of the research presented in this report with the research on metal and organic contaminants in the Lower Mississippi River will provide an understanding of how natural organic substances affect contaminant transport and transformations.

Acknowledgments

The data presented in this report are the result of a group effort in sampling the Mississippi River and some of its tributaries, processing the samples to fractionate and isolate the various dissolved and sediment phases, and sharing data and assisting in data interpretation.

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We also wish to acknowledge the Mississippi River project chief, Robert H. Meade, who along with John Moody, attempted to teach a boatload of chemists the fundamentals of surface-water hydrology.

Lastly, we wish to acknowledge our colleagues who assisted in measuring river discharge, collecting and processing large volumes of water for water and sediment sampling, performing field and laboratory measurements, and performing miscellaneous boat operations. These people include Ronald C. Antweiler, LaDonna M. Bishop, Terry I. Brinton, Gregory K. Brown, Wesley L. Campbell, Goeff S. Ellis, John R. Garbarino, Donald A. Goolsby, Heidi Hayes, Robert M. Hirsch, Donald Kelley, Jim Krest, Gail E. Mallard, Richard Martin, Stephanie G. Monsterleet, Dale B. Peart, Ronald E. Rathbun, Alan M. Shiller, John F. Sullivan, David Roth, Charles F. Tabor, Howard E. Taylor, Woodrow Wang, Harold Weigner, and Jeffrey H. Writer.

JUNE-AUGUST 1991 CRUISE

Objectives and Approach

Following are the objectives of the first sampling cruise. (1) Increase volume of water processed through the centrifuge and ultrafilter from 100 L used in the previous Mississippi River studies (Leenheer and others, 1989; Leenheer and others, 1995) to 500 to 1,000 L to obtain sufficient suspended silt, clays, and colloids for organic-car-

bon and nitrogen analyses from the navigation pools of the Upper Mississippi River where suspended sediment concentrations are much less than in the Lower Mississippi River. (2) Obtain composite bed-sediment samples from transects across the lower portions of the navigation pools for organic-carbon and nitrogen analyses. (3) Obtain high-resolution dissolved organic-carbon (DOC) data (samples taken from mid-channel approximately every 16.1 km) on the upriver part of the cruise.

The water samples obtained for DOC analyses during the upriver part of the cruise were collected from just below the water surface with a stainless-steel bucket. The samples were filtered through a 1- μ m glass fiber filter and were preserved by refrigeration. The large-volume samples (500 to 1,000 L) taken on the downriver part of the cruise were collected by pumping discharge-weighted volumes of water from 5 m below the surface or one-half the water depth at 4 to 40 locations across the river and combining suspended sediments in these samples into one pumped composite sample. This pumping method was found to undersample the suspended sand (>63 μ m) but to collect a representative sample of the suspended silt and clay fraction (< 63 μ m) (Moody and Meade, 1994). This sample was then sequentially passed through a sieve to separate the sand fraction, through a continuous-flow centrifuge to separate the suspended silt and clay, and finally through a tangential-flow ultrafilter to separate the colloid fraction (Leenheer and others, 1989). Silts and clays from the centrifuge and colloids from the ultrafilter were composited into separate "pumped-composite" fractions.

Some modifications were made to previous procedures (Leenheer and others, 1989) to obtain better recoveries of the silt and clay and colloid fractions. For the silt and clay fraction, the centrifuge housing of the drag bushing assembly was changed to capture the silts and clays that were previously lost to the sump of the centrifuge when the water drained from the bowl when the centrifuge was shut down. The water-collection area and drains in this housing were coated with Teflon to minimize contamination. When the centrifuge was shut down, the water that drained from the bowl was collected in a 2-L Teflon bottle, the coarse silt was allowed to settle, and the water was decanted. For the pumped composite samples, this coarse silt fraction was recombined with the silt recovered from the Teflon liner in the centrifuge bowl. The second procedure modification was to disassemble the bowl-bottom sealing unit of the centrifuge bowl and rinse out the silt and clay trapped in this unit. The third procedure modification was to place the Teflon liner from the centrifuge bowl inside a Teflon bag containing water that drained back from the centrifuge and to remove the accumulated silt and clay by massaging the liner surface with the inside of the Teflon bag. The previous procedure used a scraper to remove the silt. Finally, the silt suspension was allowed to settle for 1–2 weeks during storage at 4°C in the laboratory; the supernatant suspension was decanted and the silt was air dried.

For the colloid fraction, 15 ultrafilter plates were used to filter as much as 1,000 L of water. After removing the colloids from the ultrafilter plates by massaging the plates with retentate water inside a Teflon bag, the entire colloid suspension was concentrated in 1 to 2 L of retentate water. The previous procedure (Leenheer and others, 1989) used additional supercentrifugation in the laboratory to separate the colloids into a mineral colloid and an organic colloid fraction. The modified procedure freeze-dried the entire colloid suspension to obtain better recoveries.

Dissolved Organic Matter

For samples from the downriver part of the cruises, DOC concentrations were determined on a Dohrmann DC-190 carbon analyzer by high-temperature oxidation of dissolved organic carbon to carbon dioxide (Hedges and Farrington, 1993). For samples from the upriver part of the cruises, DOC concentrations were determined by persulfate oxidation of organic matter to CO_2 with an Oceanographic International Model 700 carbon analyzer (Aiken, 1992). For both of these methods for the freshwater samples from the Mississippi River, DOC was quantitatively measured after compensation for the system blanks with a precision of \pm 0.1 mg/L. DOC transport for the downriver legs were computed using water-discharge measurements reported by Moody and Meade (1994b). DOC concentrations measured on samples taken during the upriver part of the cruise are presented in table 1.

The data in table 1 show that DOC is relatively low (3.6 to 5.1 mg/L) and invariant in the Lower Mississippi River (river mile 0 to 954); whereas in the Upper Mississippi River (river mile 954 to 1800), the DOC a maximum of 14.4 mg/L at Minneapolis, Minn. Tributary inputs from the Ohio, Missouri, Illinois, Des Moines, Skunk, Iowa, and Minnesota Rivers dilute DOC concentrations in the Mississippi River. DOC concentrations in the Rock, Wisconsin, Black, and Chippewa Rivers are similar to DOC concentrations in the Mississippi River, and the St. Croix

Table 1. Dissolved organic-carbon concentrations for samples collected during the upriver part of the June–August 1991 cruise

[CDT, Central Daylight Time; mg/L, milligrams per liter]

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissolved organic carbor	
(33.1)		concentration (mg/L)	
	UPPER MISSISSIPPI RIVER		
	July 2, 1991		
2115	1,799.8	14.4	
2058	1,797.8 Minnesota River	7.3	
2008	1,791.8	9.8	
1757	1,779.9	10.3	
1614	1,766.2	9.6	
1605	1,765.3 St. Croix River	20.8	
1519	1,759.3	10.2	
1154	1,730.2	10.9	
1049	1,718.7	11.8	
1035	1,717.2 Chippewa River	12.4	
0939	1,709.3	11.9	
0535	1,689.5	12.1	
0347	1,677.0	11.6	
0133	1,663.8	12.3	
	July 1, 1991		
2359	1,652.0 Black River	12.8	
2238	1,639.9	11.6	
2123	1,629.3	11.6	
2014	1,618.5	12.2	
1855	1,606.8	12.1	
1735	1,595.6	11.6	
1634	1,586.8	12.4	
1614	1,584.4 Wisconsin River	9.9	
1329	1,563.8	11.4	
1145	1,556.0	11.3	
1030	1,544.3	11.4	
0914	1,535.3	11.3	
0813	1,525.8	11.1	
0700	1,514.5	11.2	
0555	1,504.8	10.8	
0440	1,493.6	10.5	
0340	1,484.8	10.5	
0204	1,473.8	10.3	
0056	1,463.1	10.2	

Table 1. Dissolved organic-carbon concentrations for samples collected during the upriver part of the June–August 1991 cruise --Continued

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissoived organic carbo concentration (mg/L)
	UPPER MISSISSIPPI RIVER—Continued	
	Juue 30, 1991	
2355	1,454.8	9.9
2219	1,444.9	9.9
2046	1,433.8	9.8
2035	1,432.8 Rock River	9.9
1842	1,410.9	9.3
1613	1,401.4	9.2
1349	1,387.8 Iowa River	4.3
1139	1,371.0	8.6
0620	1,356.6	8.6
0533	1,349.6 Skunk River	3.0
0405	1,335.6	7.8
0302	1,324.7	8.5
0123	1,317.7	7.4
0111	1,315.2 Des Moines River	4.3
	June 29, 1991	
2312	1,295.3	6.4
2120	1,284.8	6.9
1959	1,274.8	7.5
1842	1,263.8	7.4
1701	1,252.8	6.9
1606	1,244.8	6.4
1514	1,237.1	7.2
1257	1,225.8	6.8
1145	1,214.0	6.5
1026	1,203.0	6.6
0915	1,194.0	6.3
0802	1,183.0	6.4
0709	1,175.4	6.8
0550	1,171.7 Illinois River	4.7
0012	1,161.0	6.5
22.17	June 28, 1991	
2245	1,152.2	6.0
1945	1,149.1 Missouri River	3.6
1832	1,134.1	6.2
1706	1,123.8	4.5
1541	1,112.0	6.1

Table 1. Dissolved organic-carbon concentrations for samples collected during the upriver part of the June–August 1991 cruise --Continued

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissoived organic carbo	
······ (02 0)		concentration (mg/L)	
	UPPER MISSISSIPPI RIVER—Continued		
	June 28, 1991Continued		
1437	1,103.8	5.4	
1321	1,094.2	4.7	
1205	1,084.4	5.3	
1045	1,073.9	5.1	
0928	1,063.8	5.6	
0814	1,054.5	5.3	
0702	1,044.8	5.1	
0603	1,036.6	5.1	
0452	1,027.5	5.2	
0334	1,017.1	5.2	
0214	1,005.4	5.4	
0024	992.8	5.1	
	June 27, 1991		
2304	983.4	5.2	
2154	974.7	5.1	
2034	964.6	5.2	
1903	953.8 Ohio River	2.5	
	LOWER MISSISSIPPI RIVER		
	June 27, 1991		
1553	937.6	4.4	
1418	924.5	4.4	
1255	911.9	4.3	
1118	898.9	4.8	
1017	890.5	4.3	
0919	882.4	4.6	
0757	870.0	4.5	
0653	860.2	4.7	
0525	848.5	4.4	
0403	839.0	4.6	
0324	835.5	4.7	
0221	826.7	5.1	
0105	817.5	4.5	
	June 26, 1991		
2345	807.9	4.6	
2224	797.4	4.5	
2042	785.0	4.5	
1919	773.0	4.4	
1802	762.2	4.7	

Table 1. Dissolved organic-carbon concentrations for samples collected during the upriver part of the June–August 1991 cruise --Continued

Time (CDT)	River mlle above Head of Passes, Louisisna ¹	Dissolved organic carbo concentration (mg/L)
	LOWER MISSISSIPPI RIVER—Continued	
	June 26, 1991—Continned	
1640	751.1	4.5
1525	742.0	4.3
1248	731.5	4.4
1135	721.5	4.5
1023	712.9	4.4
0903	702.0	4.3
0725	689.9	4.4
0616	680.0	4.6
0505	669.9	4.4
0353	660.2	4.5
0241	650.2	4.4
0113	639.7	4.4
	June 25, 1991	
2314	629.3	4,4
2223	616.5	4.4
2109	610.0	4.3
1932	600.2	4.3
1834	590.3	4.2
1718	580.8	4.2
1635	575.0	4.1
1528	562.2	4.0
1420	552.5	4.1
1310	545.0	4.0
1106	534.5	4.0
1000	525.3	4.0
0837	514.1	4.1
0725	504.5	4.0
0618	493.0	4.0
0512	485.5	4.0
0400	475.0	4.1
0315	469.0	4.0
0215	460.8	4.0
0050	449.1	4.2

Table 1. Dissolved organic-carbon concentrations for samples collected during the upriver part of the June–August 1991 cruise --Continued

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissolved organic carbon
	LOWED MICCOCOUNT DIVER C. C.	concentration (mg/L)
	LOWER MISSISSIPPI RIVER—Continued Jnne 24, 1991	
2352	439.8	4.0
2259	432.0	3.9
2135	420.1	4.0
2029	409.5	4.0
	399.4	4.0
1915	399.4	4.0
1810	389.8	4.1
1704	380.4	4.1
1605	371.2	3.9
1320	360.0	4.0
1215	351.2	3.8
1105	340.0	3.8
1010	330.4	3.9
0833	320.0	3.8
0745	310.0	3.8
0640	300.0	3.7
0525	20 0 0	2.6
0525	289.8	3.6
0415	279.7	3.8
0300	269.6	3.9
0146	258.6	3.9
0045	248.8	3.9
22.17	June 23, 1991	4.5
2345	240.3	4.0
2240	230.0	4.0

¹To obtain Upper Mississippi River miles, subtract 953.8 from all river miles greater than 953.8. Tributary locations are

Mississippi River miles at mouths of tributaries.

River has DOC concentrations substantially in excess of DOC found in the Mississippi River. No DOC peaks indicative of large, organic contamination inputs are shown in table 1 data.

Data collected on the downriver part of the sampling cruise had more significance with regard to transport than the upriver part data because depth-integrated sampling was proportional to the water discharge, although sampling in the strict Lagrangian sense was not attempted and evaluated. The samples were also more representative because of the depth integration. The concentration and transport of DOC for the downstream part of the July-August 1991 cruise are given in table 2.

The water discharge data in table 2 indicates no substantial gains or losses at tributary confluences until the diversion of the Old River downstream from Vicksburg, Mississippi; thus, sampling likely occurred with reasonable adherence to Lagrangian conditions. The data in table 2 indicate a possible instream loss of DOC in the Upper Mississippi River, but no significant DOC loss in the Lower Mississippi River. This cumulative loss reaches a maximum at the Keokuk, Iowa, sampling site. The dissolved organic-carbon concentrations listed in table 2 are slightly less than those listed in table 1. These lower concentrations may result from the sample being ultrafiltered because ultrafiltration removes 10–15 percent of the DOC as colloids (Leenheer and others, 1995). It is also likely that DOC concentrations changed between the upriver and downriver legs of the sampling cruises.

Organic Matter in Suspended-Sediment Fractions

Concentrations of silt and clay and colloids were determined by physically isolating, weighing, and analyzing these fractions recovered from very large volumes of water (500 to 1000 L) passed through the continuous-flow centrifuge and ultrafilter. Organic-carbon and nitrogen analyses were performed on the recovered fractions by Huffman Laboratories, Inc., Golden, Colo. Organic carbon was determined as the difference between total carbon and carbonate carbon. Nitrogen was determined as total nitrogen that included both ammonium and organic forms of nitrogen. The maximum relative standard deviation allowed by the laboratory for replicate sediment samples was 10 percent for organic carbon and 20 percent for nitrogen. Computed concentrations for silt and clay, colloid, silt and clay organic carbon, and colloidal organic carbon are presented in table 3.

Recovery of the silt and clay plus colloid fractions ranged from 78 to 102 percent. These recoveries are defined as the concentration of the silt and clay and colloid fractions calculated for the pumped-composite sample divided by the concentration calculated for the <63-µm sediment fraction (Moody and Meade, 1994b) for the depth-integrated composite sample times 100. Sediment losses result from undersampling the coarse silt fraction with the pump sampler, losses during cleaning of the centrifuge and ultrafilter, loss from the centrifuge during the centrifuge shutdown procedure, and laboratory losses during the final drying and weighing procedure. Silt and clay concentrations vary with suspended sediment concentrations, but colloid and especially colloidal organic-carbon concentrations are relatively constant. Even the silt and clay organic-carbon concentration varies much less than the silt and clay concentration. Decreases in the silt and clay concentrations at the Pepin, Wis., and Keokuk, Iowa, sites illustrate how Lake Pepin and Pool 19 act as suspended-sediment traps.

Colloid organic-carbon concentrations that are initially 1.1 mg/L at the St. Anthony Falls, Minn., site decrease to 0.7 mg/L at the Trempealeau, Wis., site because of dilution by waters of lower colloid concentration from the Minnesota, St. Croix, and Chippewa Rivers, and then increase downriver to a maximum (0.9 mg/L) at the Keokuk, Iowa, site. The decrease in colloid organic-carbon concentrations downriver to Belle Chasse, La., results from dilution from tributaries and possible instream degradation of colloidal organic carbon. The instream degradation hypothesis is supported by colloidal organic-carbon concentration decreases at the last three sampling sites in the Lower Mississippi River where there are no significant tributary inputs to cause dilution. Salt flocculation of colloids is not a factor for this data set because these Lower Mississippi River samples were taken above the salinity gradient.

The organic-carbon and nitrogen contents of the silt and clay and colloid fractions are listed in table 4. The results are given on a dry-weight percent basis.

The organic-carbon content of the colloid fraction is three to five times as great as that of the silt and clay fraction. This feature of colloids is very important with regard to contaminant transport of nonpolar organic contaminants such as polychlorinated biphenyls (PCB's) that partition into the organic matter (Rostad and others, 1994). The greatest organic-carbon percentages on the silts and clays and colloids were recorded at sites where suspended-sediment concentrations were low. There appears to be a fractionation whereby low organic-carbon

Table 2. Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the June–August 1991 cruise

[mg/L, milligram per liter; m³/s, cubic meter per second; --, site not directly below a tributary;]

					Transport	Cumulative	percent galı
	Site name	River mlie		Dissolved	of	or loss belo	w tributary ²
Date 1991		above Water Head discharge of Passes, (m ³ /s) Louislana ¹		organic carbon concentration (mg/L)	dissolved carbon (metric tons per	Water discharga	Carbon transport
7-05	Mississippi River above	1,811.5	470	11.2	dey) 455		
, 05	St. Anthony Falls, Minn.	1,011.5	170	11.2	133		
7-06	Minnesota River at Mile 3.5, Minn.	1,797.8	600	6.6	340		
7-08	Mississippi River at Hastings, Minn.	1,766.0	980	9.1	770	-8	-3
7-08	St. Croix River at Mile 0.5, Wis.	1,765.3	260	13.5	303		
7-10	Mississippi River near Pepin, Wis.	1,718.3	1,340	9.0	1,040	+1	-5
7-10	Chippewa River at Mile 1.7, Wis.	1,717.2	170	9.8	140		
7-12	Mississippi River at Trempealeau, Wis.	1,667.6	1,440	8.6	1,100	-4	-11
7-15	Mississippi River below Lock and Dam 9, Wis.	1,593.5	1,590	7.8	1,100	+6	-11
7-15	Wisconsin River at Mile 1.0, Wisconsin	1,584.4	145	7.2	90		
7-18	Mississippi River at Clinton, Iowa	1,474.1	1,850	7.7	1,230	+12	-7
7-20	Rock River at Mile 1.0, 111.	1,432.8	70	4.0	24		
7-20	Iowa River at Mile 1.0, Iowa	1,387.8	200	2.9	50		a. 49
7-21	Mississippi River at Keokuk, Iowa	1,316.9	2,050	6.7	1,190	+7	-15
7-22	Des Moines River at Mile 1.0, Iowa	1,315.2	620	3.8	200		
7-24	Mississippi River near Winfield, Mo.	1,193.0	2,730	6.2	1,460	+8	-9
7-25	Illinois River at Hardin, Ill., Mile 21.8	1,171.7	260	4.1	92		
7-27	Missouri River at St. Charles, Mo., Mile 28.4	1,149.1	1,100	2.9	280		••
7-28	Kaskaskia River at Mile 1.5, Ill., Mile 21.8	1,071.1	7	5.1	3		

Table 2. Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the June–August 1991 cruise --Continued

					Transport	Cumulative	percent gain		
		River mlle		Dissolved	of	or loss below tributary ²			
Date	Site name	above Water Site name Head discharge		organic carbon	dissolved carbon	Medan	Carbon		
1991		of Passes,	(m^3/s)	concentration	(metric	Water			
		Louislana ¹		(mg/L)	tons per	discharge	transport		
						day)			
7-29	Mississippi River at Thebes, Ill.	997.7	4,390	5.4	2,050	+13	+4		
7-30	Ohio River at Olmsted, Ill.	953.8	2,410	2.0	420				
8-01	White River at Mile 1.2, Ark.	598.0	370	1.8	58				
8-01	Arkansas River at Mile 0.0, Ark.	581.0	480	3.6	150				
8-02	Yazoo River at Mile 3.0, Miss.	437.0	640	3.4	190				
8-03	Mississippi River below Vicksburg, Miss.	433.4	8,750	3.6	2,720	12	-3		
8-05	Mississippi River near St. Francisville, La.	266.4	6,190	3.9	2,090	-21 ³	25 ³		
8-07	Mississippi River below Belle Chasse, La.	73.1	4,340	3.8	1,420	<u>-44³</u>	-49 ³		

Tributary locations are Mississippi River miles at mouth of tributary.

²This value is the water discharge or carbon transport divided by the sum of all the inputs from tributaries upstream and Mississippi River above St. Anthony Falls, times 100.

³Flow diversion to the Old River is responsible for the cumulative percentage change.

Table 3. Concentrations of silt and clay and colloid fractions of suspended sediment and organic carbon concentrations of these fractions in samples collected during the downriver part of the June-August 1991 cruise

[Suspended sediment concentrations are reported by Moody and Meade (1994b); <, less than; µm, micrometer; mg/L, milligram per liter]

Dete	Site name	River mile above Head	Suspended sediment concentration	reco	rations of vered I frections	Recovery of silt and clay	organic (rations of cerbon of vered fractions
1991		of Passes, Louislana ¹	<63 μm (mg/L)	Slit end clay (mg/L)	Colioid (mg/L)	and colloid	Silt end clay (mg/L)	Colloid (mg/L)
7-05	Mississippi River above St. Anthony Falls, Minn.	1,811.5	30	24.8	4.1	96	1.8	1.1
7-06	Minnesota River at Mile 3.5, Minn.	1,797.8	103	80.4	5.8	84	2.3	² 0.6
7-08	Mississippi River at Hastings, Minn.	1,766.0	82	66.1	5.5	87	2.4	0.9
7-10	Mississippi River near Pepin, Wis.	1,718.3	9	5.6	3.2	98	0.5	0.7
7-12	Mississippi River at Trempealeau, Wis.	1,667.6	28	19.7	2.7	80	1.1	0.7
7-15	Mississippi River below Lock and Dam 9, Wis.	1,593.5	73	60.1	4.2	88	2.6	0.8
7-18	Mississippi River at Clinton, Iowa	1,474.1	66	53.9	3.8	87	2.4	0.9
7-21	Mississippi River at Keokuk, Iowa	1,316.9	45	34.7	3.8	86	1.9	0.9
7-24	Mississippi River near Winfield, Mo.	1,193.0	74	58.9	4.3	85	3.4	0.7
7-25	Illinois River at Hardin, Ill.	1,171.7	47	42.9	4.9	102	1.3	0.8
7-27	Missouri River at St. Charles, Mo.	1,149.1	108	95.6	5.1	93	2.1	0.4
7-29	Mississippi River at Thebes, Ill.	997.7	82	67.7	4.8	88	2.0	0.6
7-30	Ohio River at Olmsted, Ill.	953.8	22	14.5	2.6	78	0.6	0.6
8-03	Mississippi River below Vicksburg, Miss.	433.4	108	92.8	4.9	90	1.9	0.4
8-05	Mississippi River near St. Francisville, La.	266.4	112	95.4	4.6	89	1.8	0.4
8-07	Mississippi River below Belle Chasse, La.	73.1	42	31.5	3.1	82	0.8	0.2

¹Tributary locations are Mississippi River miles at mouths of tributaries.

²Average of duplicate analyses.

Table 4. Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment in samples collected during the downriver part of the June-August 1991 cruise

[C, carbon; N, nitrogen]

·		Silt	Silt and clay fraction			Colloid fraction		
Date 1991	Site name	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio (percent)	
7-05	Mississippi River above St. Anthony Falls, Minn.	7.7	1.0	8.8	27	2.9	10.7	
7-06	Minnesota River at Mile 3.5, Minn.	2.9	0.3	10.5	10	1.7	7.1	
7-08	Mississippi River at Hastings, Minn.	3.6	0.5	8.6	16	2.1	8.5	
7-10	Mississippi River near Pepin, Wis.	8.9	1.3	8.1	22	2.7	9.4	
7-12	Mississippi River at Trempealeau, Wis.	5.6	0.8	8.3	26	3.0	9.7	
7-15	Mississippi River below Lock and Dam 9, Wis.	4.3	0.6	8.5	19	2.4	8.9	
7-18	Mississippi River at Clinton, Iowa	4.5	0.7	7.3	24	3.1	8.5	
7-21	Mississippi River at Keokuk, Iowa	5.5	0.9	7.0	24	3.7	7.9	
7-24	Mississippi River near Winfield, Mo.	4.6	0.7	7.2	16	2.3	8.4	
7-25	Illinois River at Hardin, Ill.	3.0	0.5	7.8	16	2.3	8.7	
7-27	Missouri River at St. Charles, Mo.	2.2	0.3	8.3	8	1.0	8.2	
7-29	Mississippi River at Thebes, Ill.	3.0	0.5	7.6	12	1.8	8.5	
7-30	Ohio River at Olmsted, Ill.	4.1	0.7	7.3	23	3.2	8.1	
8-03	Mississippi River below Vicksburg, Miss.	2.0	0.3	8.5	8	1.0	9.6	
8-05	Mississippi River near St. Francisville, La.	2.0	0.3	9.1	9	0.9	8.8	
8-07	Mississippi River below Belle Chasse, La.	2.5	0.3	11.4	6	1.0	8.6	

clay colloids flocculated into silt-sized aggregates and are removed by sedimentation processes. Organic matter is known to disperse clay colloids so that they do not flocculate into larger particles (Frenkel and others, 1992).

In the lower Mississippi River, instream degradation of organic matter on the silt and colloid fractions might be indicated by decreasing carbon contents and increasing ratios of carbon to nitrogen. However, inputs of low-carbon sediments from the Missouri River and the analytical errors associated with the nitrogen determination may be alternative explanations for these observed changes in the lower Mississippi River.

The data in tables 3 and 4 were used to calculate transport of organic carbon and nitrogen in the silt and colloidal phases. These results are shown in table 5.

Major transport of organic carbon and nitrogen on the silt and clay fraction came from the Des Moines and Arkansas Rivers. However, most of this transport was lost, apparently by sedimentation and instream degradation of organic matter, by the time the river passed Belle Chasse, La. Further measurements are necessary to verify the hypothesis about instream degradation of organic matter during transport because the river was not sampled in a perfect Lagrangian manner during the downriver cruises.

A major portion of the colloid organic-carbon and nitrogen transport in the Upper Mississippi River is in the reach between Trempealeau, Wis., and Winfield, Mo. Where sediment concentrations are low (Mississippi River near Pepin, Wis., and the Ohio River at Olmsted, Ill., table 3), the organic-carbon and nitrogen transport are approximately equally distributed between the silt and clay and colloid fractions (table 5). For this particular cruise, the Upper Mississippi River contributed more organic carbon and nitrogen on the silt and clay and colloids to the Lower Mississippi River than did the Missouri, Ohio, and Arkansas Rivers. The water discharge of the Upper Mississippi River also was greater than the discharge of the Missouri, Ohio, and Arkansas Rivers during this sampling.

SEPTEMBER-NOVEMBER 1991 CRUISE

Objectives and Approach

The objectives were the same as in the first sampling cruise. The timing of this cruise enabled sampling of the Mississippi River during the low-water period and cooler temperature period of the fall. Presumably, the hydrologic and water temperature differences of the fall cruise as compared to the previous summer cruise would affect the quantity and quality of organic substances in the Mississippi River. In addition, the hydrophobic portion of the DOC was qualitatively assessed by isolating it from the ultrafiltered water samples on board the ACADIANA, and determining the ¹H-NMR spectra of this DOC in the laboratory.

Dissolved Organic Matter

The hydrophobic portion of dissolved organic carbon was isolated by adsorption chromatography on XAD-8 resin. Ultrafiltered water was acidified pH 2 with hydrolochloric acid, and then the acidified water was passed through a column packed with XAD-8 resin on board the ACADIANA. The column was eluted with methanol, and the HCl was neutralized with sodium bicarbonate to prevent the formation of methyl esters of DOC. In the laboratory, methanol was removed by vacuum evaporation, the DOC was reconcentrated on and eluted from an XAD-8 column to remove residual salts, and ¹H-NMR spectra of this DOC were determined to characterize the DOC. DOC concentrations measured on samples collected during the upriver part of the sampling cruise are presented in table 6.

The downriver gains in water discharge in table 7 indicate nonadherence to Lagrangian sampling during the low water discharges of this cruise. Consequently, the data on dissolved organic carbon transport cannot be clearly interpreted with respect to instream gains or losses.

The downriver DOC concentrations in table 7 generally are greater than the upriver DOC concentrations in table 6. This difference illustrates changes during the elapsed time in sampling the river between the upriver and downriver parts of the cruise.

Table 5. Organic-carbon and nitrogen transport on the silt and clay and colloid fractions for sediment samples collected during the downriver part of the June-August 1991 cruise

[Water discharge data used to compute transport are reported by Moody and Meade, 1994b]

		Water	Transport or	silt and clay	Transport on colloids	
Date 1991	Site name	Water discharge (cubic meters per second)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)
7-05	Mississippi River above St. Anthony Falls, Minn.	470	77	10	45	5
7-06	Minnesota River at Mile 3.5, Minn.	600	120	14	31	5
7-08	Mississippi River at Hastings, Minn.	980	200	28	76	10
7-10	Mississippi River near Pepin, Wis.	1,350	58	8	82	10
7-12	Mississippi River at Trempealeau, Wis.	1,440	140	20	87	10
7-15	Mississippi River below Lock and Dam 9, Wis.	1,590	360	49	110	14
7-18	Mississippi River at Clinton, Iowa	1,850	380	58	140	19
7-21	Mississippi River at Keokuk, Iowa	2,050	340	56	160	25
7-24	Mississippi River near Winfield, Mo.	2,730	640	100	170	23
7-25	Illinois River at Hardin, Ill.	260	29	4	18	2
7-27	Missouri River at St. Charles, Mo.	1,100	200	28	38	5
7-29	Mississippi River at Thebes, Ill.	4,390	760	120	230	33
7-30	Ohio River at Olmsted, Ill.	2,410	120	20	120	17
8-03	Mississippi River below Vicksburg, Miss.	8,750	1,400	180	300	38
8-05	Mississippi River near St. Francisville, La.	6,180	1,000	130	210	23
8-07	Mississippi River below Belle Chasse, La.	4,340	300	30	75	8

Table 6. Dissolved organic-carbon concentrations for samples during the upriver part of the September–November 1991 cruise listed in downriver order

[CDT, Central Daylight Time; mg/L, milligram per liter; --, no measurement]

Time (CDT)	Time (CDT) River mile ebove Head of Pesses, Louisiana ¹	
		concentration (mg/L)
	UPPER MISSISSIPPI RIVER	
	October 4, 1991	
2213	1,799.8	10.5
2155	1,797.8 Minnesota River	7.7
2023	1,791.8	9.7
1900	1,779.9	9.7
1729	1,766.3	9.9
1720	1,765.3 St. Croix River	12.1
1642	1,759.3	10.6
1520	1,746.9	10.3
1431	1,740.0	10.5
1319	1,730.2	10.4
1215	1,718.3	10.0
1108	1,709.3	10.1
0902	1,699.3	9.7
0545	1,689.5	9.4
0410	1,667.0	9.3
0316	1,652.0 Black River	7.7
0121	1,653.8	9.0
	October 3, 1991	
2313	1,639.9	8.8
2050	1,619.3	8.6
1932	1,606.8	8.4
1807	1,595.6	8.4
1703	1,586.8	8.2
1645	1,584.4 Wisconsin River	7.7
1548	1,575.1	8.2
1412	1,563.8	8.2
1246	1,556.0	8.1
1131	1,544.3	8.2
0904	1,535.3	8.2
0805	1,525.8	8.1
0656	1,514.5	8.2
0537	1,504.8	8.0
0248	1,484.8	8.0
0016	1,463.1	7.8

Table 6. Dissolved organic-carbon concentrations for samples during the upriver part of the September–November 1991 cruise listed in downriver order --Continued

Time (CDT)	River mile above Heed of Passes, Louisiana ¹	Dissoived organic-cerbo
(02.)		concentration (mg/L)
	UPPER MISSISSIPPI RIVER—Continued	
	October 2, 1991	
2322	1,455.8	7.9
2141	1,444.8	7.7
2013	1,433.8	7.8
2005	1,432.8 Rock River	6.7
1837	1,418.8	7.9
1720	1,409.8	8.0
1626	1,400.8	7.8
1413	1,388.8	7.8
1321	1,380.8	7.8
1218	1,371.8	7.2
0928	1,360.8	7.7
0532	1,350.8	7.6
0347	1,335.8	7.7
0245	1,324.8	7.7
0136	1,316.8	7.6
0118	1,315.2 Des Moines River	7.7
0000	1,304.8	7.7
	October 1, 1991	
2212	1,294.8	7.6
2107	1,284.8	7.6
1852	1,274.8	7.5
1740	1,263.8	7.7
1553	1,253.3	7.7
1504	1,245.8	7.7
1407	1,237.1	7.6
1225	1,225.8	7.5
1109	1,214.0	7.4
1000	1,203.0	7.4
0700	1,194.0	7.3
0600	1,184.3	7.4
0507	1,175.4	7.3
0415	1,171.7 Illinois River	4.8
0253	1,161.0	7.0
0127	1,152.2	6.9

Table 6. Dissolved organic-carbon concentrations for samples during the upriver part of the September–November 1991 cruise listed in downriver order --Continued

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissolved organic-carbor
Time (CDT)	niver fille above fleau of Passes, Louisiana	concentration (mg/L)
	UPPER MISSISSIPPI RIVER—Continned	
	September 30, 1991	
2333	1,149.1 Missouri River	3.1
2139	1,134.1	5.5
1835	1,108.8	5.7
1521	1,082.7	5.8
1222	1,058.3	5.5
0924	1,034.6	5.5
0823	1,027.5	5.5
0712	1,017.4	5.5
0550	1,005.4	5.5
0413	992.8	5.5
0315	984.6	5.5
0148	973.6	5.5
0039	964.6	5.6
	September 29, 1991	
2121	953.8 Ohio River	2.7
	LOWER MISSISSIPPI RIVER	
2029	950.5	4.8
1715	922.6	4.6
1419	898.9	4.5
1121	875.4	4.3
1010	866.5	4.4
0852	855.0	4.4
0752	846.5	4.4
0610	833.6	4.6
0350	814.8	4.6
0234	804.5	4.5
0124	795.5	4.5
2344	783.0	4.4
2240	773.0	4.5
2036	762.2	4.4
1920	751.1	4.4
1811	742.0	4.4
1546	731.5	4.4
1436	721.5	4.3
1327	712.9	4,3

Table 6. Dissolved organic-carbon concentrations for samples during the upriver part of the September–November 1991 cruise listed in downriver order --Continued

Time (CDT)	River mile above Head of Passes, Louisisns ¹	Dissoived organic-carbon
	TOTALDA ACONOCIDADO NATURA	concentration (mg/L)
	LOWER MISSISSIPPI RIVER-Continued September 29, 1991, Continued	
1200	September 29, 1991—Continued 702.0	4.3
1031	689.9	4.3
0858	679.4	4.3
0752	669.9	4.3
0640	660.2	4.3
0040	000.2	7.5
0527	650.2	4.3
0427	641.7	4.4
0252	629.3	4.3
0122	617.7	4.2
0047	608.8	4.2
	September 27, 1991	
2309	601,0	4.2
2111	590.3	4.1
1957	580.8	4.2
1750	562.8	4.1
1630	551.8	4.0
1544	545.0	4.0
1335	534.5	4.1
1225	524.9	4.0
1059	514.1	3.9
0953	504.5	3.9
0825	493.0	3.8
0730	485.2	3.8
0615	474.5	3.8
0433	460.8	3.8
0312	449.2	3.7
0208	439.8	3.8
0114	432.0	3.7
22.5	September 26, 1991	
2345	420.1	3.8
2235	409.5	3.8
2111	398.8	3.8
2007	389.6	3.8
1900	380.5	3.8

Table 6. Dissolved organic-carbon concentrations for samples during the upriver part of the September–November 1991 cruise listed in downriver order --Continued

Time (CDT)	River mile above Head of Passes, Louisisna ¹	Dissoived organic-csrbon
	LOWER MISSISSIPPI RIVER-Continued	concentration (mg/L)
	September 26, 1991—Continued	
1704	371.2	3.7
1555	360.0	3.7
1447	351.3	3.7
1334	340.0	3.6
1229	330.4	3.6
1128	321.1	3.5
1019	310.0	3.6
	September 26, 1991	
0924	301.0	3.5
0758	289.6	3.5
0655	279.7	3.4
0545	269.9	3.8
0435	258.8	3.4
0337	249.0	3.6
0241	240.0	4.3
	September 25, 1991	
2120	230.0	3.7
1950	216.2	3.7
1850	206.8	3.7
1742	195.1	3.6
1635	184.8	3.6
1532	175.4	3.6
1430	164.7	3.7
1325	155.6	3.6
1235	145.0	3.7
1126	134.9	3.6
1019	123.1	3.7
0922	113.9	3.8
0853	105.1	
	September 25, 1991	
0757	99.1	4.1
0647	88.5	4.1

¹To obtain Upper Mississippi River miles, subtract 953.8 from all river miles greater than 953.8. Tributary locations are

Mississippi River miles at mouths of tributaries.

Table 7. Dissolved organic carbon concentrations and transport for samples collected during the downriver part of the September-November 1991 cruise

[Dashes indicate sites that are not directly below a tributary; mg/L, milligram per liter; m³/s, cubic meter per second]

		···· • • • • • • • • • • • • • • • • •		······································	Transport	Cumulative percent gain	
		River mile Dissolved			of	or loss below tributary ²	
Date 1991	Site name	above Head of Passes, Louisiana ¹	organic carbon concentration (mg/L)	Water disch a rge (m³/s)	dissolved organic carbon (metric tons per day)	Water discharge	Carbon transport
10-07	Mississippi River above St. Anthony Falls, Minn.	1,811.5	8.5	220	160		
10-08	Minnesota River at Mile 3.5, Minn.	1,797.8	7.4	130	83		
10-10	Mississippi River at Hastings, Minn.	1,766.0	9.2	350	280	0	+15
10-10	St. Croix River at Mile 0.5, Wis.	1,765.3	15.3	95	130		
10-13	Mississippi River near Pepin, Wis.	1,718.3	11.3	510	500	+15	+34
10-13	Chippewa River at Mile 1.7, Wis.	1,717.2	11.0	150	140		
10-15	Mississippi River at Trempealeau, Wis.	1,667.6	10.9	660	620	+11	+21
10-18	Mississippi River below Lock and Dam 9, Wis.	1,593.5	8.3	690	500	+16	-3
10-18	Wisconsin River at Mile 1.0, Wis.	1,584.4	5.1	160	71	**	
10-22	Mississippi River at Clinton, Iowa	1,474.1	8.7	940	710	+25	+22
10-26	Rock River at Mile 1.0, Ill.	1,432.8	5.3	80	36		
10-26	Iowa River at Mile 1.0, Iowa	1,387.8	4.0	70	24		
10-27	Mississippi River at Keokuk, Iowa	1,316.9	6.0	1,410	730	+56	+14
10-28	Des Moines River at Mile 1.0, Iowa	1,315.2	4.5	80	31		
10-30	Mississippi River near Winfield, Mo.	1,193.0	7.6	1,230	810	+25	+21
10-31	Illinois River at Hardin, Ill.	1,171.7	4.2	520	190		
11-03	Missouri River at St. Charles, Mo.	1,149.1	3.9	1,350	450		
11-05	Mississippi River at Thebes, Ill.	997.7	5.4	3,870	1,810	+35	+38
11-06	Ohio River at Olmsted, Ill.	953.8	3.0	2,480	640		

Table 7. Dissolved organic carbon concentrations and transport for samples collected during the downriver part of the September–November 1991 cruise --Continued

					Transport	Cumulative	percent gain
		River mile	Dissolved		of	or loss below tributary ²	
Date 1991	Site name	above Head of Passes, Louisiana ¹	organic carbon concentration (mg/L)	Water discharge (m ³ /s)	dissoived organic carbon (metric tons per day)	Water discharge	Carbon transport
11-07	White River at Mile 1.2, Ark.	598.0	3.8	1,210	400		
i1-07	Arkansas River at Mile 0.0, Ark.	581.0	4.6	1,620	640		
11-08	Yazoo River at Mile 3.0, Miss.	437.0	3.6	540	170		
11-09	Mississippi River below Vicksburg, Miss.	433.4	4.3	10,700	4,000	+26	+25
1[-11	Mississippi River near St. Francisville, La.	266,4	3.7	8,950	2,900	+5 ³	_9 ³
11-13	Mississippi River below Belle Chasse, La.	73.1	4.8	8,840	3,700	+4 ³	+163

¹Tributary locations are Mississippi River miles at mouth of tributary.

²This value is the water discharge or carbon transport divided by the sum of all the inputs from tributaries upstream times 100.

³Flow diversion to the Old River is responsible for the cumulative percentage change.

Organic Matter in Suspended-Sediment Fractions

Concentrations of silt and clay and colloids were isolated, weighed, and analyzed in the same manner as on the previous downriver part of the June-August 1991 sampling cruise. These data and organic carbon concentrations are presented in table 8.

Recovery of the silt and clay, and colloid fractions ranged from 82 to 111 percent. The mean recovery was 92 percent. A similar pattern of recoveries as a function of the sampling site was observed during this cruise (September-November 1991) and the June-August 1991 cruise (tables 3 and 8).

Suspended-sediment concentrations were very low in the Upper Mississippi River during this period of low water discharge, but colloid and colloidal organic-carbon concentrations generally were similar to those for the previous sampling during the June-August 1991 cruise. Most of the sediment input during the September-November 1991 cruise was from the Missouri and Arkansas Rivers. Suspended-sediment concentrations were significantly greater in the Lower Mississippi River during the September-November 1991 cruise than during the June-August 1991 cruise, but colloidal organic-carbon concentrations were only slightly greater. The colloidal organic-carbon concentrations were generally lower in the Lower Mississippi River than in the Upper Mississippi River.

The organic-carbon and nitrogen composition of the silt and colloid fractions is listed in table 9. The results are given on a dry-weight percent basis.

The data in table 9 are notable for the exceptionally low C:N ratios in the silt and clay fraction and the high organic-carbon percentages in the colloid fraction. The minimum silt and clay C:N ratio is at the Keokuk, Iowa, site as it was for the summer sampling cruise (table 4). The low water discharge and low suspended-sediment conditions that existed in the Upper Mississippi River during September—November 1991 resulted in silt and clay with exceptionally high nitrogen content and colloids with exceptionally high organic-carbon content.

The transport calculations in table 10 show that relatively small quantities of organic carbon are transported in the Upper Mississippi River. Large increases in the organic-carbon and nitrogen loads at the Vicksburg, Miss., St. Francisville, La., and Belle Chasse, La., sites probably are caused by high water discharge and high suspended-sediment inputs from the White and Arkansas Rivers.

MARCH-MAY 1992 CRUISE

Objectives

The major objective of this sampling cruise was to repeat the studies of the previous two cruises under hydrologic and climatic conditions that exist in the spring. An early ice breakup on the navigation pools of the Upper Mississippi River made it possible to complete the upriver trip on schedule and begin the downriver trip at Minneapolis, Minnesota, by April 7, 1992.

Dissolved Organic Matter

Dissolved organic-carbon concentrations measured in water samples collected during the upriver part of the March-May 1992 cruise are presented in table 11. The DOC data in table 11 are the lowest DOC concentrations of the upriver sampling cruises. The early snow melt and runoff from tributaries in Wisconsin and Minnesota caused a water-discharge pulse in the Upper Mississippi River that was encountered just north of St. Louis (river mile 1200) during the upriver sampling cruise; however, this discharge pulse was not accompanied by a DOC pulse resulting from snowmelt, but rather a slight dilution of DOC was observed.

The DOC concentrations and transport determined from samples taken during the downriver leg are listed in table 12. Low water discharges occurred from Minneapolis downstream to Clinton, Iowa. However, the Iowa River and later the Missouri River were running "bank full", and inputs from these tributaries dramatically increased the water discharge and sediment concentrations for the remainder of the downstream sampling.

The DOC concentration data for the downriver part of the March-May 1992 cruise in table 12 were similar to the DOC concentration data for the upriver part in table 11 with a few exceptions. The high discharge of low DOC water from the Des Moines, Iowa, and Rock rivers diluted the DOC in the Mississippi River, whereas the

Table 8. Concentrations of silt and clay and colloid fractions of suspended sediment and organic-carbon concentrations of these fractions for samples collected on the downiver part of the September–November 1991 cruise

[Suspended sediment concentrations are reported by Moody and Meade (1994b); <, less than; µm, micrometer; mg/L, milligram per liter]

Date	Suspended River mile sediment above Head Site name of Passes, Louisisns (mg/L)	above Head Site name		Concentrations of recovered sediment fractions		Recovery of silt and cisy	Concentrations of organic carbon of recovered sediment fractions	
1991		Silt snd clay (mg/L)	Coiloid (mg/L)	colioid (percant)	Siit snd ciay (mg/L)	Colloid (mg/L)		
10-07	Mississippi River above St. Anthony Falls, Minn.	1,811.5	12	7.2	3.9	92	1.0	1.2
10-08	Minnesota River at Mile 3.5, Minn.	1,797.8	62	52.3	5.7	94	3.0	0.9
10-10	Mississippi River at Hastings, Minn.	1,766.0	45	41.3	4.6	102	2.7	1.0
10-13	Mississippi River near Pepin, Wis.	1,718.3	9	5.0	2.4	82	0.5	0.7
10-15	Mississippi River at Trempealeau, Wis.	1,667.6	12	7.9	2.6	88	0.9	0.7
10-18	Mississippi River below Lock and Dam 9, Wis.	1,593.5	28	20.4	4.5	89	1.5	0.8
10-22	Mississippi River at Clinton, Iowa	1,474.1	31	24.2	3.7	90	1.5	0.7
10-27	Mississippi River at Keokuk, Iowa	1,316.9	32	25.7	3.9	92	1.6	0.8
10-30	Mississippi River near Winfield, Mo.	1,193.0	36	30.4	5.0	98	1.7	0.8
10-31	Illinois River at Hardin, Ill., Mile 21.8	1,171.7	143	147.3	11.2	111	² 2.7	1.2
11-03	Missouri River at St. Charles, Mo.	1,149.1	163	137.2	8.1	89	2.8	0.5
11-05	Mississippi River at Thebes, Ill.	997.7	80	66.3	6.7	91	1.9	0.7
11-06	Ohio River at Olmsted, Ill.	953.8	19	13.3	2.8	85	0.5	0.4
11-09	Mississippi River below Vicksburg, Miss.	433.4	154	128.8	10.5	90	1.9	0.6
11-11	Mississippi River near St. Francisville, La.	266.4	172	135.6	12.6	86	3.0	0.7
11-13	Mississippi River below Belle Chasse, La.	73.1	112	85.3	9.9	85	1.3	0,5

¹Tributary locations are Mississippi River miles at mouths of tributaries.

²Average of duplicate analyses.

Table 9. Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment for samples collected on the downriver part of the September-November 1991 cruise

[C, carbon; N, nitrogen]

		Silt and clay fraction			Colloid fraction			
Data 1991	Site name	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio	Organic carbon (percent)	Nitrogan (percent)	Atomic C:N ratio (percent)	
10-07	Mississippi River above St. Anthony Falls, Minn.	13	2.2	7.3	28	2.9	12.4	
10-08	Minnesota River at Mile 3.5, Minn.	5.7	1.0	7.0	16	1.8	9.8	
10-10	Mississippi River at Hastings, Minn.	6.5	1.0	7.3	22	2.4	10.5	
10-13	Mississippi River near Pepin, Wis.	10	1.9	6.9	29	2.3	13.4	
10-15	Mississippi River at Trempealeau, Wis.	11	1.9	6.9	27	3.0	9.3	
10-18	Mississippi River below Lock and Dam 9, Wis.	11	1.3	6.9	27	2.2	8.5	
10-22	Mississippi River at Clinton, Iowa	6.2	1.0	7.0	19	2.2	8.5	
10-27	Mississippi River at Keokuk, Iowa	6.2	1.1	6.5	21	2.4	8.5	
10-30	Mississippi River near Winfield, Mo.	5.6	0.9	7.2	16	2.0	8.2	
10-31	Illînois River at Hardin, Ill.	1.8	0.3	8.5	11	1.3	7.9	
11-03	Missouri River at St. Charles, Mo.	2.0	0.3	7.3	6.2	0.9	7.4	
11-05	Mississippi River at Thebes, Ill.	2.9	0.5	7.3	12	1.3	10.0	
11-06	Ohio River at Olmsted, Ill.	3.8	0.5	7.6	14	1.7	9.3	
11-09	Mississippi River below Vicksburg, Miss.	1.6	0.2	7.3	5.7	0.8	7.6	
11-11	Mississippi River near St. Francisville, La.	2.3	0.3	9.2	5.6	0.8	7.6	
11-13	Mississippi River below Belle Chasse, La.	1.5	0.2	7.2	5.1	0.7	8.5	

Table 10. Organic-carbon and nitrogen transport on the silt and clay and colloid fractions for sediment samples collected on the downriver part of the September-November 1991 cruise

[Water discharge data used to compute transport are reported by Moody and Meade, 1994b]

		14/240	Transport or	silt and clay	Transport on colloids		
Date 1991	Site name	Water discharge (cubic meters per second)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tona per day)	
10-07	Mississippi River above St. Anthony Falls, Minn.	220	19	3	21	2	
10-08	Minnesota River at Mile 3.5, Minn.	130	34	5	10	1	
10-10	Mississippi River at Hastings, Minn.	350	82	13	82	3	
10-13	Mississippi River near Pepin, Wis.	510	22	4	31	2	
10-15	Mississippi River at Trempealeau, Wis.	660	51	8	40	4	
10-18	Mississippi River below Lock and Dam 9, Wis.	690	130	23	72	9	
10-22	Mississippi River at Clinton, Iowa	940	120	20	57	7	
10-27	Mississippi River at Keokuk, Iowa	1,140	160	35	79	11	
10-30	Mississippi River near Winfield, Mo.	1,230	180	30	85	11	
10-31	Illinois River at Hardin, Ill.	520	120	16	54	7	
11-03	Missouri River at St. Charles, Mo.	1,350	330	45	58	8	
11-05	Mississippi River at Thebes, Ill.	3,870	640	100	270	32	
11-06	Ohio River at Olmsted, Ill.	2,480	110	15	86	10	
11-09	Mississippi River below Vicksburg, Miss.	10,700	1,800	250	550	75	
11-11	Mississippi River near St. Francisville, La.	8,950	2,400	310	540	75	
11-13	Mississippi River below Belle Chasse, La.	8,840	990	140	380	53	

Table 11. Dissolved organic carbon concentrations for samples collected during the upriver part of the March–May 1992 cruise listed in downriver order

[CDT, Central Daylight Time; mg/L, milligram per liter; --, no measurement]

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissolved organic-carbo concentration (mg/L)
	TIDDED MOOTOOTDE DATA	
	UPPER MISSISSIPPI RIVER April 4, 1991	
0733	1,799.4	9.6
0711	1,797.8 Minnesota River	6.5
0548	1,788.9	8.3
0304	1,779.9	7.9
0117	1,766.8	8.0
0103	1,765.3 St. Croix River	9.6
0015	1,759.3	8.6
0015	April 3, 1992	0.0
2210	1,746.9	8.3
2107	1,730.2	8.5
2005	1,718.3	8.6
1953	1,717.2 Chippewa River	8.3
1859	1,709.3	8.5
1726	1,699.3	8.1
1614	1,689.5	8.2
1449	1,677.4	8.0
1307	1,663.3	8.3
1116	1,649.9	8.2
0955	1,638.1	8.1
0813	1,623.7	8.0
0628	1,606.8	7.8
0532	1,598.7	7.4
0406	1,585.7	7.3
0356	1,584.4 Wisconsin River	7.5
0245	1,574.8	7.3
0120	1,563.8	7.3
	April 2, 1992	
2237	1,550.8	7.1
2046	1,535.3	7.3
1951	1,526.7	7.2
1838	1,515.1	7.2
1716	1,502.8	7.1

Table 11. Dissolved organic carbon concentrations for samples collected during the upriver part of the March–May 1992 cruise listed in downriver order --Continued

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissolved organic-carbo
	niver time above nead of Passes, Louisiana	concentration (mg/L)
	UPPER MISSISSIPPI RIVER—Continued	
	April 2, 1991—Continued	
1530	1,486.8	6.9
1403	1,473.8	6.9
1228	1,460.2	6.9
1031	1,444.5	6.9
0908	1,435.4	6.8
0838	1,432.8 Rock River	6.3
0650	1,416.6	6.7
0539	1,406.8	6.8
0307	1,387.8 Iowa River	6.6
0156	1,378.8	6.5
0035	1,366.8	6.5
	April 1, 1992	
2121	1,356.8	6.5
1 9 48	1,341.8	6.7
1823	1,327.8	6.8
1620	1,315.5	6.1
1615	1,315.2 Des Moines River	3.9
1437	1,300.8	6.3
1311	1,289.8	5.4
1143	1,278.4	5.9
0943	1,260.8	5.7
0745	1,246.8	6.1
0630	1,236.4	6.0
0454	1,223.8	5.7
0250	1,212.3	5.6
0123	1,199.8	5.8
· -	March 31, 1992	
2248	1,187.3	5.7
2125	1,174.8	6.0
2035	1,171.7 Illinois River	4.4
1850	1,160.9	5.9
1717	1,152.1	5.9
1554	1,149.1 Missouri River	4.9
1405	1,134.1	5.3
1229	1,123.5	5.3
0903	1,099.5	4.9

Table 11. Dissolved organic carbon concentrations for samples collected during the upriver part of the March–May 1992 cruise listed in downriver order --Continued

Time (CDT)	River mile above Head of Passes, Louisiana ¹	Dissolved organic-carbo
		concentration (mg/L)
	UPPER MISSIPPI RIVER—Continued	
0629	March 31, 1992—Continned 1,081.5	5.1
0450	1,071.1 Kaskaskia River	7.3
0340	•	7.3 5.2
0143	1,063.6	
0143	1,050.0 March 30, 1991	5.1
2346	1,034.3	5.2
2138	1,019.2	5.1
1920	1,003.2	5.2
1719	988.1	5.1
1528	973.6	5.1
1422	965.4	5.2
1246	953.8 Ohio River	2.8
	LOWER MISSISSIPPI RIVER	
1047	950.5	4.4
0713	923.0	3.8
0400	898.9	4.0
0107	878.1	4.0
	March 29, 1991	
2105	848.0	3.9
1926	837.4	3.8
1810	828.0	3.9
1644	815.8	3.8
1513	804.7	3.8
1356	795.5	3.9
1227	784.6	3.8
1103	774.0	4.0
0940	763.0	4.0
0820	752.9	3.9
0640	742.0	3.8
0544	735.0	3.8
0143	723.3	3.9
0029	714.3	4.1
_	March 28, 1992	
2308	705.0	3.9
2138	695.0	3.9
2011	683.4	3.8
1843	672.7	3.8

Table 11. Dissolved organic carbon concentrations for samples collected during the upriver part of the March–May 1992 cruise listed in downriver order --Continued

Time (CDT)	River mile above Heed of Passes, Louisiana ¹	Dissolved organic-carbo
111110 (OD1)	inter time above fided of Fasses, Louisidild	concentration (mg/L)
	LOWER MISSISSIPPI RIVER—Continued	
	March 28, 1992—Continued	
1659	659.8	3.8
1540	650.1	3.6
1401	638.7	3.8
1229	626.6	3.6
1040	614.1	3.7
0858	602.0	3.8
0734	592.1	3.6
0613	582.0	3.7
0550	581.0 Arkansas River	4.2
0317	565.1	3.7
0139	555.0	3.6
0009	544.9	3.5
0007	March 27, 1992	3.5
2128	535.0	3.6
1951	525.0	3.6
1823	514.1	3.6
1651	504.5	3.6
1001	March 27, 1992	
1532	495.1	3.6
1410	485.5	3.6
1246	475.0	3.6
1121	464.8	3.7
0957	454.3	3.6
0847	445.2	3.7
0729	435.3	3.7
0531	421.8	3.6
0402	409.5	3.6
0234	399.4	3.7
0117	389.8	3.6
0019	380.0	3.5
	March 26, 1992	
2252	371.2	3.1
2011	360.0	3.5
1853	351.3	3.5
1731	340.0	3.4
1620	330.4	3.5

Table 11. Dissolved organic carbon concentrations for samples collected during the upriver part of the March–May 1992 cruise listed in downriver order --Continued

Time (ODT)	Diver wile shave Head of Decree 1 autota-1	Dissolved organic-carbon
Time (CDT)	River mile above Head of Passes, Louisiana ¹	concentration (mg/L)
	LOWER MISSISSIPPI RIVER—Continued	
	March 26, 1992—Continued	
1515	321.1	3.5
1354	310.0	3.5
1243	300.0	3.4
1131	290.0	3.5
1018	280.0	3.6
0907	270.0	3.5
0804	260.8	3.5
0647	250.0	3.4
0532	240.3	3.5
	March 25, 1992	
2348	228.0	3.4
2236	220.0	3.4
2124	210.0	3.3
2011	200.0	3.4
1900	190.0	3.3
1752	179.5	3.3
1649	170.0	3.2
1539	160.1	3.3
1424	149.7	3.2
1312	139.8	3.2
1205	130.0	3.3
1044	119.0	3.3
0938	110.0	3.3
0829	100.0	3.2
0705	90.0	3.3

¹To obtain Upper Mississippi River miles, subtract 953.8 from all river miles greater than 953.8. Tributary locations are

Mississippi River miles at mouths of tributaries.

Table 12. Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the March—May 1992 cruise

[Dashes indicate sites that are not directly below a tributary; mg/L, milligram per liter; and m³/s, cubic meter per second]

					Transport of	Cumulative percent gain or toaa below tributary ²	
Date 1991	Site name	River mile above Head of Passes, Louisiana ¹	Dissolved organic carbon concentration (mg/L)	Water discharge (m³/s)	dissolved organic carbon (metric tons per	Watar discharga	Carbon traneport
4-06	Mississippi River above St. Anthony Falls, Minn.	1,811.5	10.6	310	284		••
4-08	Minnesota River at Mile 3.5, Minn.	1,797.8	6.2	260	140		
4-10	Mississippi River at Hastings, Minn.	1,766.0	7.6	570	374	0	-12
4-11	St. Croix River at Mile 0.5, Wis.	1,765.3	6.7	320	185		
4-12	Mississippi River near Pepin, Wis.	1,718.3	7.5	950	615	+7	+1
4-12	Chippewa River at Mile 1.7, Wis.	1,717.2	6.9	300	179		***
4-14	Mississippi River at Trempealeau, Wis.	1,667.6	6.8	1,330	781	+12	-1
4-17	Mississippi River below Lock and Dam 9, Wis.	1,593.5	6.3	1,590	865	+34	+10
4-17	Wisconsin River at Mile 1.0, Wis.	1,584.4	5.6	889	655		
4-19	Mississippi River at Clinton, Iowa	1,474.1	6.4	2,320	1,283	+12	-11
4-22	Rock River at Mile 1.0, Ill.	1,432.8	2.3	340	68		
4-22	Iowa River at Mile 1.0, Iowa	1,387.8	3.1	680	182	••	
4-23	Mississippi River at Keokuk, Iowa	1,316.9	4.9	4,220	1,786	+36	5
4-24	Des Moines River at Mile 1.0, Iowa	1,315.2	3.8	730	240		••
4-26	Mississippi River near Winfield, Mo.	1,193.0	4.8	5,070	2,103	+32	+9
4-27	Illinois River at Hardin, Ill.	1,171.7	3.5	860	260		***
4-29	Missouri River at St. Charles, Mo.	1,149.1	9.0	3,560	2,768	~~	
4-30	Kaskaskia River at Mile 1.5, Ill.	1,071.1	5.9	30	15	••	

Table 12. Dissolved organic-carbon concentrations and transport for samples collected during the downriver part of the March—May 1992 cruise --Continued

					Transport	Cumulative	percent gain
		River mile Dissoived			of	or loss below tributary ²	
Date 1991	Site name	above Head of Passes, Louisiana	organic carbon concentration (mg/L)	Water discharge (m³/s)	dissolved organic carbon (metric tons per	Water discharge	Carbon tranaport
5-01	Mississippi River at Thebes, Ill.	997.7	5.1	10,500	4,620	+27	- 7
5-03	Ohio River at Olmsted, Ill.	953.8	2.0	6,150	1,060		
5-04	White River at Mile 1.2, Ark.	598.0	2.2	920	175		••
5-04	Arkansas River at Mile 0.0, Ark.	581.0	6.2	710	380		
5-05	Yazoo River at Mile 3.0, Miss.	437.0	3.2	70	19		
5-06	Mississippi River below Vicksburg, Miss.	433.4	3.0	21,800	5,640	+35	-15
5-08	Mississippi River near St. Francisville, La.	266.4	2.7	15,100	3,520	-6 ³	-47 ³
5-10	Mississippi River below Belle Chasse, La.	73.1	3.0	14,500	3,760	-10^{3}	-43 ³

¹Tributary locations are Mississippi River miles at mouth of tributary.

²This value is the water discharge or carbon transport divided by the sum of all the inputs from tributaries upstream times 100.

³Flow diversion to the Old River is responsible for the cumulative percentage change.

high discharge in the Missouri River was accompanied by a high DOC that enriched the DOC in the Mississippi River.

The difference in cumulative percentages below tributary confluences between water discharge percentage in minus DOC transport percentage are consistently negative. This negative mass balance is a possible indication of instream degradation of DOC, although the positive bias in the mass balance data of water discharge indicates that same parcel of water was not being consistently sampled downstream, and variations in DOC concentrations between different parcels of water can also explain this data set.

Organic Matter in Suspended-Sediment Fractions

Silt and clay and colloids were isolated, weighed, and analyzed in the same manner as on the previous down-river cruises. The data are presented in table 13.

The high water discharge and suspended-sediment concentrations in the Iowa and Missouri Rivers caused large increases in the suspended-silt and clay concentrations in the Mississippi River (table 13). Only slight increases in colloidal organic-carbon concentrations were observed with large increases in suspended-silt and clay concentrations. The constancy of the colloidal organic-carbon concentrations is remarkable, considering the large variations in suspended-sediment concentrations during this sampling cruise.

The organic-carbon and nitrogen composition of the silt and colloid fractions is listed in table 14. The results are given on a dry-weight percent basis.

The most notable feature of the compositional data in table 14 is the abrupt decrease in organic carbon and nitrogen percentages of the silt and clay and colloid fractions in the Mississippi River as high concentrations of suspended sediment from the Iowa River and the Missouri River enter the Mississippi River. The atomic C:N ratio generally appears to vary inversely among sampling locations between the silt and clay, and colloid fractions. The atomic C:N ratio of the colloid fraction at Keokuk, Iowa, is especially low (7.9).

The data in tables 13 and 14 and were used to calculate transport of organic carbon and nitrogen in the silt and clay and colloidal phases. These results are shown in table 15.

The organic carbon and nitrogen transport for the silt and clay fraction in the Mississippi River show large increases at the Keokuk and Thebes, Ill., sites because of large sediment inputs from the Iowa and Missouri Rivers. The transport downriver from these tributaries are the largest measured for any of the three sampling cruises. The magnitude of the increase in organic carbon and nitrogen loads of the colloids at the Keokuk and Thebes sites is much less than the increases for the silt fractions at these sites.

ORGANIC MATTER IN BED SEDIMENTS

Bed sediments were sampled and composited for the lower portion of the navigation pools. The specific locations, method of sampling, and method of compositing are given in the report to be published as an Open-File Report by the U.S. Geological Survey titled "Hydrologic, sedimentologic and chemical data describing water and bed sediments in the navigation pools of the Upper Mississippi River, July 1991-April 1992. In addition, bed-sediment samples were taken in the Lower Mississippi River and certain tributaries at sites where fine sediments accumulated (behind wing dams and bridge abutments). The organic-carbon and nitrogen contents of these bed-sediment samples are listed in table 16.

The contents of organic carbon and nitrogen in the bed sediments are much lower than in the suspended silt and clay and colloid fractions because of the presence of inorganic sands in the bed sediments. The bed-sediment samples with the greatest organic-carbon content are from Lower Lake Pepin (Pool 4), which is the most efficient sediment trap for fine-grained and high organic-carbon sediments on the Upper Mississippi River.

The atomic C:N ratio is one indicator of the trophic status of the bed sediments; low C:N ratios indicate incomplete biological decomposition of organic nitrogen and ammonia in eutrophic bed sediments. Lake Pepin, Pool 19, Pool 22, Pool 24, and the site near Thebes, Ill., all have low C:N ratios that may indicate excess nitrogen in bed sediments. This excess nitrogen may result in ammonia production in sediment pore waters during periods of low oxygen and high biological activity. The Pig's Eye Slough sample has a low C:N ratio because this sample was taken just below the outfall of the Minneapolis-St. Paul sewage-treatment plant.

A comparison of the organic-carbon and nitrogen contents of bed-sediment samples with suspended silt and clay samples that were collected in close proximity to each other is given in table 17.

Table 13. Concentrations of silt and clay and colloid fractions of suspended sediment and organic-carbon concentrations of these fractions for samples collected on the downriver part of the March–May 1992 cruise

[Suspended sediment concentrations are reported by Moody and Meade (1994b); <, less than; µm, micrometer; mg/L, milligram per liter]

Dste	Site nsme	River mile sbove Head	Suspended sediment concentration	reco	rations of vered fractions	Recovery of silt snd cisy	cisy (r (mg/L) (r 1.3 2.5 1.9 0.9 1.0 1.4 1.9	carbon of vered
1991		of Passes, Louisiana ¹	<63 μm (mg/L)	Siit snd clay (mg/L)	Colloid (mg/L)	coilold		Collold (mg/L)
4-06	Mississippi River above St. Anthony Falls, Minn.	1,811.5	12	7.7	0.9	72	1.3	0.1
4-0 8	Minnesota River at Mile 3.5, Minn.	1,797.8	96	89.6	5.8	99	2.5	0.8
4-10	Mississippi River at Hastings, Minn.	1,766.0	36	29.7	4.6	95	1,9	0.9
4-12	Mississippi River near Pepin, Wis.	1,718.3	12	8.1	3.2	94	0.9	0.9
4-14	Mississippi River at Trempealeau, Wis,	1,667.6	14	10.1	3.4	96	1.0	0.9
4-17	Mississippi River below Lock and Dam 9, Wis.	1,593.5	24	19.4	3.2	94	1.4	0.8
4-19	Mississippi River at Clinton, Iowa	1,474.1	40	31.0	3.9	87	1.9	0.9
4-23	Mississippi River at Keokuk, Iowa	1,316.9	299	132	15.6	49	3.5	1.1
4-26	Mississippi River near Winfield, Mo.	1,193.0	293	200	13.7	73	4.8	² 1.1
4-27	Illinois River at Hardin, Ill.	1,171.7	230	256	9.4	115	5.2	0.8
4-29	Missouri River at St. Charles, Mo.	1,149.1	1,180	1,146	36.6	100	14.4	1.5
5-01	Mississippi River at Thebes, Ill.	997.7	600	577	20.7	100	8.5	1.1
5-03	Ohio River at Olmsted, Ill.	953.8	67	58.4	4.6	94	1.4	0.5
5-06	Mississippi River below Vicksburg, Miss.	433.4	300	275	17.8	98		0.9
5-08	Mississippi River near St. Francisville, La.	266.4	297	240	17.0	87	4.3	0.8
5-10	Mississippi River below Belle Chasse, La.	73.1	303	248	17.1	87	4.4	0.8

¹Tributary locations are Mississippi River miles at mouths of tributaries.

²Average of duplicate analyses.

Table 14. Organic-carbon and nitrogen contents of silt and clay and colloid fractions of suspended sediment for samples collected on the downriver part of the March–May 1992 cruise

[C, carbon; N, nitrogen]

		Silt and clay fraction			Colloid fraction		
Date 1991	Site name	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio	Organic carbon (percent)	Nitrogen (percent)	Atomic C:N ratio (percent)
4-06	Mississippi River above St. Anthony Falls, Minn.	17	2.9	6.8	11	1.6	10.2
4-08	Minnesota River at Mile 3.5, Minn.	2.8	0.5	7.0	14	1.9	8.8
4-10	Mississippi River at Hastings, Minn.	6.4	1.1	6.6	20	2.4	9.5
4-12	Mississippi River near Pepin, Wis.	11	1.9	6.9	28	3.3	9.6
4-14	Mississippi River at Trempealeau, Wis.	9.9	1.6	7.3	26	2.7	11.2
4-17	Mississippi River below Lock and Dam 9, Wis.	7.2	1.3	6.8	25	2.7	11.2
4-19	Mississippi River at Clinton, Iowa	6.1	1.0	7.0	23	2.5	10.9
4-23	Mississippi River at Keokuk, Iowa	2.7	0.3	10.5	7.1	1.1	7.9
4-26	Mississippi River near Winfield, Mo.	2.4	0.3	10.0	8.0	1.0	9.3
4-27	Illinois River at Hardin, Ill.	2.0	0.2	10.7	9.6	1.3	8.1
4-29	Missouri River at St. Charles, Mo.	1.3	0.1	13.4	4.1	0.5	10.2
5-01	Mississippi River at Thebes, Ill.	1.5	0.2	10.3	5.3	0.7	8.1
5-03	Ohio River at Olmsted, Ill.	2.4	0.3	10.0	11	1.3	8.2
5-06	Mississippi River below Vicksburg, Miss.	1.8	0.2	10.3	5.1	0.6	9.4
5-08	Mississippi River near St. Francisville, La.	1.8	0.2	10.4	4.7	0.6	9.6
5-10	Mississippi River below Belle Chasse, La.	1.8	0.2	10.8	4.7	0.6	9.7

Table 15. Organic-carbon and nitrogen transport on the silt and clay and colloid fractions for sediment samples collected on the downriver part of the March-May 1992 cruise

[Water discharge data used to compute transport are reported by Moody and Meade, 1994b]

		30/-4	Transport or	silt and clay	Transport	on colloids
Date 1991	Site name	Water discharge (cubic meters per second)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)	Organic carbon (metric tons per day)	Nitrogen (metric tons per day)
4-06	Mississippi River above St. Anthony Falls, Minn.	310	35	6	3	0.4
4-08	Minnesota River at Mile 3.5, Minn.	260	56	9	18	2
4-10	Mississippi River at Hastings, Minn.	570	94	17	44	6
4-12	Mississippi River near Pepin, Wis.	950	74	13	74	9
4-14	Mississippi River at Trempealeau, Wis.	1,330	110	18	100	11
4-17	Mississippi River below Lock and Dam 9, Wis.	1,590	190	34	110	12
4-19	Mississippi River at Clinton, Iowa	2,320	381	64	180	18
4-23	Mississippi River at Keokuk, Iowa	4,220	1,300	140	400	61
4-26	Mississippi River near Winfield, Mo.	5,070	2,100	250	480	60
4-27	Illinois River at Hardin, Ill.	860	390	42	67	9
4-29	Missouri River at St. Charles, Mo.	3,560	4,430	390	460	53
5-01	Mississippi River at Thebes, Ill.	10,500	7,710	870	1,000	120
5-03	Ohio River at Olmsted, Ill.	6,150	740	84	270	32
5-06	Mississippi River below Vicksburg, Miss.	21,800	9,200	1,030	1,700	200
5-08	Mississippi River near St. Francisville, La.	15,100	5,600	630	1,000	130
5-10	Mississippi River below Belle Chasse, La.	14,500	5,500	580	1,000	120

Table 16. Organic-carbon and nitrogen contents of bed-sediment samples

[ND, not determined; %, percent]

Location	Date	River mile ¹	Organic carbon	Nitrogen (%)	Atomic C:N
Pool 1	7-04-91	UM 848.0-849.2	(%) ND	0.0	ND
	10-08-91	UM 833.4	1.1	0.0	6.2
Pig's Eye Slough Pool 2	7-07-91	UM816.1-821.1	1.1	0.2	² 13.6
F001 2	10-09-91	UNIO10.1-021.1	1.4	0.1	ND
	4-09-92		1.4	0.1	ND
Pool 3	10-11-91	UM 797.3-798.1	1.9	0.2	11.8
Pool 4 (Upper Lake Pepin)	10-11-91	UM 774.0-778.0	3.0	0.4	8.1
Pool 4 (Lower Lake Pepin) ³	10-12-91	UM 768.0-772.0	3.5	0.4	9.7
Pool 5	7-11-91	UM 739.8-744.7	1.0	0.1	11.0
Pool 5A	7-11-91	UM 729.8	1.7	0.1	16.1
Pool 6 ³	4-13-92	UM 714.9-721.1	0.4	0.0	10.1
Pool 7	7-13-91	UM 702.7	0.7	0.1	10.5
Pool 8	7-14-91	UM 682.1-684.7	0.8	0.1	13.0
	4-16-92		0.7	0.1	ND
Pool 9	10-19-91	UM 648.0-655.0	1,0	0.1	9.9
Pool 10	7-16-91	UM 615.0-617.2	1,7	0.1	14.1
Pool 11	10-20-91	UM 585,1-591.9	0.9	0.1	9.3
Pool 12	4-18-92	UM 558,2-560.7	2.0	0.2	13.9
Pool 13 ³	10-21-91	UM 523.7-526.0	0.9	0.1	11.9
Pool 14	7-19-91	UM 494.8-499.8	0.7	0.1	9.8
Pool 15 ³	4-20-92	UM 484.0-487.8	0.7	0.1	13.4
Pool 16	10-24-91	UM 457.0-458.7	0.9	0.1	10.3
Pool 18	4-22-92	UM 411.8-414.5	1.6	0.1	14.5
Pool 19 ³	10-26-91	UM 366.3-371.6	1.2	0.2	7.5
Pool 20 ³	7-22-91	UM 344.2-346.6	0.6	0.0	14.2
Pool 21 ³	4-24-92	UM 326.6-331.4	0.5	0.0	18.7
Pool 22 ³	7-23-91	UM 303.0-306.0	0.4	0.1	6.7
Pool 24	10-29-91	UM 273.4-275.3	0.5	0.1	8.8
Pool 25	4-25-92	UM 241.5-243.1	1.5	0.1	13.6
Pool 26	11-01-91	UM 206.1	1.5	0.2	11.7
Illinois River near Hardin, Ill.	10-31-91	IL 21.8	1.6	0.2	12.4
Missouri River near St. Charles, Mo.	4-29-92	MO 28.4	0.6	0.1	11.7
Mississippi River near Thebes, Ill.	11-05-91	UM 44.0	1.5	0.2	7.5
Mississippi River near Greenville, Miss.	11-08-91	LM 566.0	0.9	0.1	13.3
Mississippi River near St. Francisville, La.	11-11-91	LM 266.4	1.3	0.1	11.9

Table 16. Organic-carbon and nitrogen contents of bed-sediment samples -- Continued

[ND, not determined; %, percent]

			Organic	N. 13.4	44! - O-N
Location	Date	River mlie ¹	carbon (%)	Nitrogen (%)	Atomic C:N ratio
Mississippi River near Belle Chasse, La.	11-13-91	LM 73.1	0.8	0.1	12.3

TUM, Upper Mississippi River miles measured upstream from the confluence with Ohio River. IL, Illinois River miles measured upstream from the confluence with Mississippi River (UM 217.9). MO, Missouri River miles measured upstream from the confluence with Mississippi River (UM 195.3). LM, Lower Mississippi River miles measured upstream from Head of Passes, Louisiana.

²Data are the mean of three samples.

³Data are the mean of two replicates.

Table 17. Organic-carbon and nitrogen percentages of bed-sediment samples and suspended silt and clay samples

Dotos	Comple and site	Organic carbon	Mitroson	Atomic carbon
Dates	Sample and site	Organic carbon	Nitrogen	to nitrogen ratio
10-11-91	Bed sediment from Pool 3	1.9	0.2	11.8
	Silt and clay from Mississippi River at Hastings, Minn. ¹	5.5	0.9	7.5
10-12, 14-91	Bed sediment from Pool 4 (Lake Pepin) ²	3.2	0.4	8.9
	Silt and clay from Mississippi River near Pepin, Wis. ¹	10.0	1.7	7.3
4-13-92	Bed sediment from Pool 6	0.4	0.0	10.1
	Silt and clay from Mississippi River at Trempealeau, Wis. ¹	8.8	.1.4	7.5
10-19-91	Bed sediment from Pool 9	1.0	0.1	9.9
	Silt and clay from Mississippi River below Lock and Dam 9, Wis. ¹	7.5	1.1	7.4
10-21-91	Bed sediment from Pool 13	0.9	0.1	11.9
	Silt and clay from Mississippi River at Clinton, Iowa ¹	5.6	0.9	7.1
10-26-91	Bed sediment from Pool 19	1.2	0.2	7.5
	Silt and clay from Mississippi River at Keokuk, Iowa ¹	4.8	0.8	8.0
4-25-92	Bed sediment from Pool 25	1.5	0.1	13.6
	Silt and clay from Mississippi River near Winfield, Mo. 1	4.2	0.6	8.1
11-05-91	Bed sediment from Mississippi River at	1.5	0.2	7.5
	Thebes, Ill. Silt and clay from Mississippi River at Thebes, Ill. 1	2.5	0.4	8.4
11-08-91	Bed sediment from Mississippi River near	0.9	0.1	13.3
	Greenville, Miss.	1.8	0.2	8.7
	Silt and clay from Mississippi River below Vicksburg, Mississippi 1			,
11-11-91	Bed sediment from Mississippi River near	1.3	0.1	11.9
	St. Francisville, La.	2.0	0.3	9.6
	Silt and clay from Mississippi River near St. Francisville, La. 1			
11-13-91	Bed sediment from Mississippi River below	0.8	0.1	12.3
	Belle Chasse, La. ¹ Silt and clay from Mississippi River below Belle Chasse, La. ¹	1.9	0.2	9.8

¹Values are means of three suspended-silt and -clay samples collected during the three sampling cruises from a site near where the bed-sediment sample was collected.

²Values are means of Upper and Lower Lake Pepin samples.

The C:N ratios of organic matter in the bed sediment is normally 3-5 units greater than the C:N ratios of suspended silts and clay because diagenetic processes normally mineralize nitrogen faster than carbon when suspended sediments are deposited in bed sediments (Ishiwatari, 1985). However, there is little difference in the C:N ratios of the bed sediment and suspended silt and clay at the Keokuk and Thebes sites, and only a small difference at Lake Pepin. These small differences may indicate particulate nitrogen is being input into the bed sediments faster than diagenetic processes degrade the nitrogen. This situation may indicate problems with sediment quality at these sites, especially if anaerobic conditions in the bed sediment produce ammonia that is toxic to organisms that live in bed sediments. Pool 19 near Keokuk is a repository for sediments contaminated with nitrogenous wastes from the Rock Island, Ill., Moline, Ill., Davenport, Iowa, and Bettendorf, Iowa, metropolitan region; it also receives agricultural nitrogenous inputs from the Iowa River. The Thebes site receives nitrogenous wastes from the St. Louis metropolitan region, and Lake Pepin receives nitrogenous wastes from Minneapolis-St. Paul region.

The suspended silts and clays become progressively depleted in organic carbon and nitrogen downstream. This depletion may represent both instream degradation of organic matter in the silt and clay fractions as they move downriver and dilution by input of silt and clay low in organic carbon by tributaries in the Lower Mississippi River. Increases in the C:N ratio of the silt and clay fraction in the Lower Mississippi River may indicate instream degradation as the sediments are transported downstream.

SEASONAL VARIATION

Dissolved Organic Matter

The dissolved organic-carbon data for the upriver of the June-August 1991 (summer), September-November (fall), and March-May 1992 (spring) sampling cruises are listed in tables 1, 6, and 11 and are shown as a function of river mile in figure 2 to assess differences in DOC between summer, fall, and spring. The water-temperature data (Moody, 1994) are also plotted in this figure to show potential differences in biological processes that generally are proportional to temperature.

The DOC data in figure 2 are nearly identical for all three cruises for the Mississippi River below the Ohio River. Upriver from the Missouri River confluence, the data begin to diverge, and marked differences are present upriver from the Des Moines River confluence. The data in table 2 indicate that there was instream loss of DOC in the Upper Mississippi River during the summer downriver cruise, but similar losses were not apparent in the data for the spring and fall downriver cruises (tables 7 and 12).

A companion study to this report on the Lower Mississippi River (Leenheer and others, 1995) used ¹H-NMR spectroscopy to qualitatively assess instream degradation of DOC. A sample ¹H-NMR spectrum of DOC isolated from the Mississippi River at Hastings, Minn., during the spring sampling cruise is shown in figure 3. In the Lower Mississippi River study, the height ratio of peak 2 to peak 1 (spectral peaks are numbered in fig. 3) was inversely related to the degree of degradation of DOC, and the ratio of peak 5 to peak 1 was directly related to the relative aromatic carbon content of the DOC. These peak height ratios for the fall and spring sampling cruises are presented in table 18.

The ratio of peaks 2:1 data in table 18 indicate that the DOC generally (excepting the sample at St. Anthony Falls) was more degraded during the fall cruise than during the spring cruise. From Lock and Dam 9 downriver, there was more degradation of DOC in the downriver direction during the fall cruise than during the spring cruise. These findings are not surprising when one considers the stream temperature profiles in figure 2. The warmer stream temperatures during the fall cruise would promote greater biological activity, and river temperature rose in a downriver direction for both spring and fall cruises.

The relative aromatic carbon content (ratio of peaks 5:1) was similar during the fall and spring cruises. Sites where there were low suspended-sediment concentrations appear to have the greatest aromatic carbon contents. Sedimentary material has been found to adsorb and act as a solubility control on aromatic humic substances in certain environments (McKnight and others, 1992). The question of whether DOC degrades instream is important with regard to contaminant transport and release. In the summer when water temperatures are near 25°C, instream degradation of DOC is hypothesized from the data in table 18 to be a significant process in the Upper Mississippi

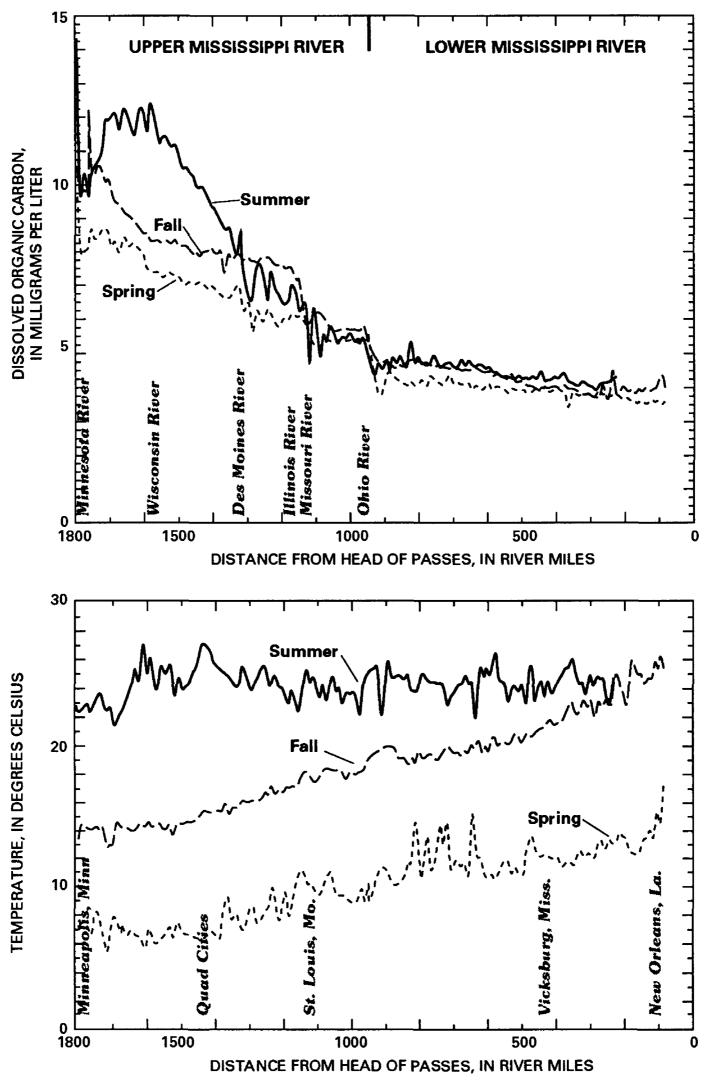


Figure 2.--Graphs showing dissolved organic-carbon concentration and water temperature (Moody, 1994) for the Mississippi River as a function of river miles upstream from Head of Passes, La., for the summer, fall, and spring. This does not show the true distance between samples in the water which is listed in a report by Moody (1994).

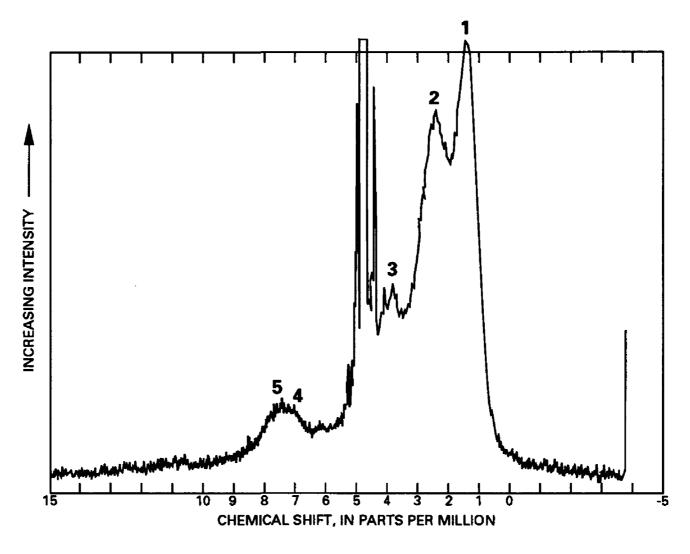


Figure 3.--¹H-nuclear magnetic resonance (NMR) spectrum of dissolved organic matter isolated from the Mississippi River at Hastings, Minn., during the March–May 1992 (spring) sampling cruise. (see text for description of numbers on spectral peaks).

Table 18. Peak height ratios for ¹H-NMR data for dissolved organic-carbon samples collected during the September-November 1991 (fall) and March-May 1992 (spring) sampling cruises

[ND, not determined]

,	September-N	o∨ember 1991	March-May 1992		
Olla mama	cru	cruise			
Site name	Peaks	Peaks	Peaks	Peaks	
	2:1	5:1	2:1	5:1	
Mississippi River above St. Anthony Falls, Minn.	0.66	0.23	1.08	0.22	
Minnesota River at River Mile 3.5, Minn.	0.66	0.10	0.77	0.13	
Mississippi River at Hastings, Minn.	0.76	0.14	0.83	0.14	
St. Croix River at River Mile 0.5, Wis.	ND	ND	0.86	0.18	
Mississippi River near Pepin, Wis.	0.77	0.18	0.86	0.18	
Mississippi River at Trempealeau, Wis.	0.83	0.19	ND	ND	
Mississippi River below Lock and Dam 9, Wis.	0.88	0.23	0.84	0.19	
Mississippi River at Clinton, Iowa	0.75	0.17	ND	ND	
Mississippi River at Keokuk, Iowa	0.69	0.14	0.83	0.19	
Mississippi River near Winfield, Mo.	0.79	0.16	ND	ND	
Illinois River at Hardin, Ill.	0.62	0.13	ND	ND	
Missouri River at St. Charles, Mo.	0.62	0.13	0.83	0.16	
Mississippi River at Thebes, Ill.	0.62	0.11	0.79	0.17	
Ohio River at Olmsted, Ill.	0.67	0.18	0.74	0.16	
Mississippi River below Vicksburg, Miss.	0.61	0.15	0.71	0.14	
Mississippi River near St. Francisville, La.	0.61	0.15	0.76	0.14	
Mississippi River below Belle Chasse, La.	ND	ND	0.67	0.15	

River. In the spring (and most likely the winter), instream degradation is minor in the Upper Mississippi River; these degradation processes are probably more important downstream where water temperatures are warmer.

Although this report presents evidence for instream degradation of DOC, examination of the spatial profiles of DOC during the three sampling cruises and examination of all relevant data presented in this report indicate that dilution of the Mississippi River by lower DOC water from southern tributaries is the major factor in causing the decrease in DOC concentrations from upstream to downstream. The reason for the lower DOC levels in the southern Mississippi River tributaries is probably the combined result of increased biodegradation rates in the soils caused by the higher annual temperatures in the South then in the North and a difference in geology and soil characteristics. The highly weathered and oxidized soils of the South are much better adsorbents for DOC (on iron and aluminum sequioxide coatings) than are the relatively young glaciated soils of the North. The Northern States also have extensive sandy glacial outwash deposits, and these sandy soils have very little affinity for dissolved organic carbon. The "black-water" tributaries of the Mississippi (Black and St. Croix Rivers) arise in the sandy-soil regions of northern Wisconsin.

Organic Matter in Suspended-Sediment Fractions

Seasonal effects are more difficult to interpret for the suspended-sediment fractions. Hydrologic processes are a larger factor in controlling suspended-sediment concentrations and composition than are biological processes that are dependent on temperature. The atomic C:N ratio of suspended sediment was found to have a seasonal dependence. In the St. Lawrence River, lower C:N ratios during the summer occur because of growth of algae that are rich in nitrogen (Telang and others, 1991). However, even the lowest C:N values in the St. Lawrence River were above typical values found for suspended sediment in the Upper Mississippi River. The C:N ratios for suspended silt and clay in the Upper Mississippi River were even lower during the low-water conditions of the fall and spring cruises than during the summer cruise when algae growth should be a significant factor.

In short, the Upper Mississippi River does not show normal seasonal geochemical trends with respect to C:N ratios of suspended sediment. A likely reason is that massive allochthonous inputs of sedimentary nitrogen from agricultural sources in Illinois, Iowa, and Minnesota dominate the more normal seasonal trends that were observed in the St. Lawrence River.

CONCLUSIONS

The four major conclusions based on the study described in this report are as follows:

- 1. Sediments in the Upper Mississippi River have large nitrogen contents. The suspended silts and clays in particular have nitrogen percentages that are 1.5 to 2.0 times those measured for natural uncontaminated sediments. These sediments probably are from areas of intensive agriculture with associated nitrogen fertilization of soils in the Upper Midwest. The likely consequence of long-term inputs of high nitrogen sediments into the navigation pools of the Upper Mississippi River is the generation of toxic levels ammonia in bed sediments during periods of high microbiological activity.
- 2. Colloidal organic matter (and possibly associated contaminants) is transported in a physically and chemically conservative manner in the Upper Mississippi River. Transport calculations indicate very little of the colloidal organic matter is being lost in the deeper navigation pools (Lake Pepin and Pool 19) that serve as sediment traps. Thus, colloid-bound contaminants may be transported conservatively in the Upper Mississippi River if the biological rate of colloid degradation is slow relative to colloid transport rates.
- 3. The large organic-carbon content of colloids in the Upper Mississippi River enhances the sorption of non-polar organic contaminants. Organic-carbon contents of the colloid fractions in the Upper Mississippi River were 2 to 3 times the contents in the Lower Mississippi River. Contaminants such as PCBs were found to partion into the organic matter of these colloids (Rostad and others, 1994) and presumably are conservatively transported on the colloids.
- 4. Dissolved, suspended silt and clay, and colloidal organic matter in the Mississippi River decreases from Minneapolis-St. Paul to New Orleans. This decrease is primarily caused by dilution from tributaries that are lower in dissolved and suspended organic-matter concentrations in the Southern United States. However, changes in

organic-matter composition and cumulative transport calculations indicate that instream loss of dissolved and colloidal organic matter occurs during transport from north to south. This loss of organic matter is of concern because associated contaminants may be released during the process of degradation. Thus, contaminants bound in the Upper Mississippi River may be transported and released in the Lower Mississippi River.

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